# Effluent Polishing by Filtration Through Activated Alumina

## Volume I

## Research Report No. 39

Research Report No. 39 Effluent Polishing by Filtration Through Activated Alumina Volume I

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search Program for the Abatement of Municipal Pollution
under Provisions of the Canada-Ontario Agreement
on Great Lakes Water Quality

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# EFFLUENT POLISHING BY FILTRATION THROUGH ACTIVATED ALUMINA

VOLUME I

(March, 1974)

by

Pollutech Pollution Advisory Services Ltd.
Oakville, Ontario

RESEARCH PROGRAM FOR THE ABATEMENT
OF MUNICIPAL POLLUTION WITHIN THE
PROVISIONS OF THE CANADA-ONTARIO
AGREEMENT ON GREAT LAKES WATER QUALITY

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# ABSTRACT

The effluent from the Oakville Water Pollution Control Plant was treated with alum to reduce the phosphorus concentration to 1 or 2 mg/l. This pretreated effluent was further polished in activated alumina columns. The phosphorus concentration in the polished effluent depended on the flowrate and the feed phosphorus concentration. Levels of 0.1 mg P/l or less were obtained by this process for appreciable periods. The performance of activated alumina was restored by regeneration with sodium hydroxide after the alumina had been exhausted. This process was estimated to be more economical than alum treatment alone if the desired concentration of phosphorus in the polished effluent was less than 0.5 mg/l.

# RESUME

Les effluents de l'usine de traitement des eaux usées de Oakville ont été traités à l'alun afin d'en réduire la concentration du phosphore à 1 ou 2 mg/l, puis sur colonnes d'alumine activée. La concentration finale en phosphore était dépendante du débit et de la concentration initiale en phosphore. Ce procédé a permis d'obtenir des concentrations de phosphore égales ou inférieures à 0.1 mg/l pendant des périodes assez longues. Une fois l'alumine activée devenue inutilisable, ses capacités lui étaient rendues par régénération à l'hydroxyde de sodium. On a estimé que ce procédé était plus économique que le traitement n'utilisant que l'alun lorsqu'on désire obtenir une concentration en phosphore inférieure à 0.5 mg/l dans l'effluent final.

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# CONCLUSIONS

1. Phosphorus was removed to levels below 1 mg/l by alum precipitation in the Oakville Water Pollution Control Plant; however, a significant increase in alum dosage as well as sludge production was observed.

2. Activated alumina is capable of reducing the phosphorus concentration of secondary effluents to very low levels.

3. In this study, it was demonstrated that the combined system employing both processes is technically feasible and economically attractive if an effluent of less than 0.5 mg/l of phosphorus is required.

4. The contact time between liquid and alumina particles as well as the phosphorus concentration in the feed are significant factors in the performance of the columns.

5. The effective capacity of activated alumina is approximately 6.5 mg P/g $Al_2O_3$. Higher capacities can be achieved but only when the column operation continued beyond the 50% breakthrough point.

6. Exhausted activated alumina can be restored to its original performance by regeneration with either 1N or 2N sodium hydroxide.

7. During regeneration, an increased contact time between alumina particles and caustic seems to be more effective; however, a more detailed study is required to confirm this observation.

8. Fluctuations in the feed phosphorus concentration will not significantly affect the performance of the columns. The results of this study indicated that doubling the feed phosphorus concentration would not decrease the quality of the polished effluent for approximately 1000 bed volumes.

# RECOMMENDATIONS

The results of this laboratory study clearly indicate that the process consisting of alum precipitation followed by activated alumina polishing is technically feasible and economically attractive for phosphorus removal when concentrations below 0.5 mg/l must be achieved.

In order to confirm these results under field conditions, it is recommended that an on-site pilot plant study using chemically pretreated secondary effluent be conducted. This study would be designed to establish the following:

- the optimum method of regenerating the columns with sodium hydroxide;
- the process variables for the sodium hydroxide recovery using lime precipitation;
- refined capital and operating costs of the treatment program based on the results of an on-site pilot investigation.

Further details of the proposed study have been presented in the POLLUTECH proposal to the Federal Department of Supply and Services and the Ontario Ministry of the Environment, submitted on January 31, 1974.

# 1. INTRODUCTION

A program under the Canada-Ontario Agreement designed to reduce the growth of algae in lakes and rivers has been instituted throughout Southern Ontario. This program requires that the phosphorus concentration be reduced, either by 80% or to an average level of 1 mg/l in the final effluent from a water pollution control plant. The selection of which effluent criterion applies depends on the watershed into which the plant discharges. Studies are under way throughout the world to determine the concentration range of phosphorus which will support but not exceed the nutrient requirements for a balanced ecology. Available data indicate that much lower effluent levels of phosphorus than 1 mg/l could eventually be required. Especially in cases where the watercourse is needed for reuse without the benefit of a long retention period in the natural system, or the area has a high recreational potential, or the treated effluent is discharged into a relatively small watercourse, the need of much more complete phosphorus removal can arise.

At present, phosphorus can be removed from sewage waters by coagulation with alum, ferric chloride, or lime. These chemicals have proven effective in reducing the residual phosphorus to 1 mg/l and studies have shown that larger chemical dosages could reduce the level even more. However, the volume of sludge developed in the process increases with the coagulant dosage and this presents a disposal problem, as well as higher operating costs. Furthermore, even if the residual phosphorus could be reduced to very low levels by conventional treatment, increased capital expenditure would probably be required for final effluent polishing.

The present study is concerned with a combination of conventional phosphorus removal and effluent polishing by activated alumina. Numerous studies have shown that activated alumina removes phosphorus effectively from the waste but cost is not favourably comparable to the conventional process if all phosphorus is removed on adsorption media. If, however, the phosphorus level has been reduced to approximately 1 mg/l by conventional coagulants, the activated alumina requirements would appreciably decrease.

Pollutech Pollution Advisory Services Limited was retained under provisions of the Canada-Ontario Agreement on Great Lakes Water Quality to investigate this combined process for the removal of phosphorus to low levels in the laboratory. This report summarizes the results of the study.

## 2. OBJECTIVES

The overall objectives of this study were to determine if activated alumina would effectively reduce the phosphorus content of an alum-pretreated secondary effluent to a level below 0.5 mg/l and to estimate if such a process would be economically feasible. For investigative purposes, this study was subdivided into two phases as follows:

### Phase I

- to determine the effectiveness of the phosphorus removal process using precipitation with alum;
- to estimate the production of precipitated solids as a result of higher alum dosages;
- to evaluate the performance of activated alumina columns in removing phosphorus from alum-pretreated secondary effluent;
- to determine the effectiveness of sodium hydroxide for regenerating exhausted activated alumina.

### Phase II

- to determine the effect of contact time in the columns on the performance of activated alumina;
- to estimate the economic feasibility of the process.

## 3. TECHNICAL BACKGROUND

The removal of phosphorus from solution by activated alumina is well known, and the principal mechanism is described as ion-exchange reactions (6, 8). Surface reactions are followed by slow migration to the interior of the alumina particles; reactions in alumina column operations are revealed by plateaus (2, 5) when the phosphorus concentration in the effluent is plotted against the length of the run. Each plateau indicates a specific reaction taking place on the surface of the alumina. As the flowrate increases, the plateaus are less marked and eventually vanish completely (5).

In order for the ion-exchange reactions to take place, the alumina must be activated so that suitable anions are available for exchange. These reactions have been studied (6, 8) and the adsorption order of ions determined (4, 7). For phosphorus, Yee (10) established the technique of activating the alumina with nitric acid but Ames and Dean (1) found that the sodium hydroxide was equally effective and that alumina losses due to activation were reduced.

Alumina with various surface areas have been studied and the most economical commercial form of alumina was found to be Alcoa F-1 which has a surface area in excess of 200 square metres per gram (10). Ames and Dean (1) found that particle size was important as well as surface area; 48 - 100 mesh (finest size tested) was the most effective. The capacities of these aluminae, i.e., the milligrams of phosphorus adsorbed per gram of alumina, varied from 5.5 to 8.8: the capacity of the medium used in this study (Alcoa F-1) was determined by Yee (10) at 6.2 mg P/gm $Al_2O_3$.

In order to collect more information about the process mechanism, Yee (10), using a synthetic phosphorus solution, found that alumina preferentially removed condensed phosphates and that the orthophosphate form breaks through first. The short chain phosphates were adsorbed more effectively than the longer molecules.

The importance of magnesium and/or calcium ions in the water was shown by Ames and Dean (1), and indicated that complex ion reactions were involved. The presence of these ions improved the phosphorus removal. Similarly, changes in pH had significant effect on process performance. As the hydrogen ion concentration in the treated water was decreased, adsorption became less efficient, but below pH 3 no further effect was noted (9). At high pH values, the degree of phosphorus removal increased, but precipitation of calcium salts and subsequent degeneration of the columns was observed by Ames and Dean (1) when a synthetic secondary wastewater effluent was used.

With few exceptions, alumina-phosphorus studies have been conducted on synthetic waters. Yee (10) treated a secondary effluent and found that an upward flow and fluidized beds were required to avoid solids plugging, but even then, a loss of performance was noted, as compared to the results for feeding synthetic wastes. Ames and Dean (1) filtered secondary effluent through activated carbon before passing it through activated alumina columns, and also, like Yee (10) they noted a decrease in removal efficiency.

Yee (10) regenerated exhausted alumina with sodium hydroxide followed by reactivation with nitric acid while Ames and Dean (1) regenerated with the caustic only. Both procedures effectively restored the capacity of the alumina. The alumina losses varied from 8% (10) to 0.33% (1), and the higher figure was attributed (1) to the use of nitric acid.

Ames and Dean (1) outlined a procedure for recovering the regenerant (sodium hydroxide) by the addition of lime. This relatively inexpensive chemical precipitated the phosphorus as a sludge from the sodium hydroxide solution and the latter could then be reused to regenerate spent alumina.

## 4. PROCEDURE

### 4.1 Preparation of Feed

Secondary effluent from the Oakville Municipal Treatment Plant was transported to the laboratory in plastic lined drums. Aliquots were treated with liquid alum at six different dosages using the procedure described in the Guidelines (3) and analyzed for suspended solids and total phosphorus. From these data, the dosage of alum required to reduce the phosphorus to the desired level was estimated, and added to the entire sample. The content of the drum was mixed, and the alum floc was allowed to settle, after which the phosphorus content of the supernatant was determined. This procedure was repeated as often as necessary, until the desired phosphorus concentration was obtained. After settling overnight, the supernatant was pumped through a glass wool filter into another plastic lined drum; about 9" of liquid was left in the first drum in order to avoid floc carry-over. Phosphorus analyses were repeated on the second drum supernatant, and these analyses were reported as the influent to the activated alumina columns. A schematic diagram of the system is shown in Figure 1. In this study, four identical activated alumina columns were used.

The above feed was then pumped to the activated alumina columns through a coarse 1/4" pad of glass wool to partially block dirt and alum floc carry-over. Because of inadequate slow mixing in the alum treatment step, the flocs remained small and settled out slowly in the drums. After the first run, the glass wool pads were changed daily; ten of these plugs were analyzed for phosphorus, after eluting by boiling for two hours in acidic solution, and found to contain 0.5 to 1.0 mg phosphorus. This amount was considered negligible and was not used in phosphorus balance calculations.

## 4.2 Operation of Columns

Glass wool was placed at the bottom of the columns to prevent alumina loss (Figure 1), and a layer of porcelain chips was added to keep the glass wool in place and prevent chanelling. The alumina used was Alcoa F-1 (48-100) mesh. Fresh alumina was washed, dried, weighed, and added to the columns as an aqueous slurry. One bed volume was 33 ml - the wet volume of 30 gm activated alumina. For one sequence of tests, two columns were activated with 1N nitric acid.

The feed was designed to contain either 1 or 2 mg/l phosphorus. This objective was met within 10%. In the first run, the concentration was based on the filtered phosphorus, but all subsequent runs were based on the phosphorus in the mixed sample.

The feed was pumped to the partially fluidized columns by peristaltic pumps equipped with two heads at designed flowrates of 0.6, 1.2 or 2.4 l/hr. Because two columns operated on one pump (2 heads), adjustments were limited to the average value. In the initial run, the glass wool filter on the feed line was not changed daily, and flowrates were difficult to maintain because the alum floc and dirt carry-over clogged the glass wool at the base of the columns. Later runs were conducted at the designed rate within 0.1 l/hr until the final stages of each run when the alumina became heavily contaminated with particles and the desired flow could not be maintained by the pumps.

At regular intervals throughout a run, the effluents from the columns were analyzed for orthophosphates in the mixed sample. The feed was analyzed daily. Orthophosphate analyses (Appendix) were selected because over 90% of the phosphorus in a secondary effluent is in that form. Given the low concentrations of phosphorus in the column effluent, this difference is usually within the experimental error,

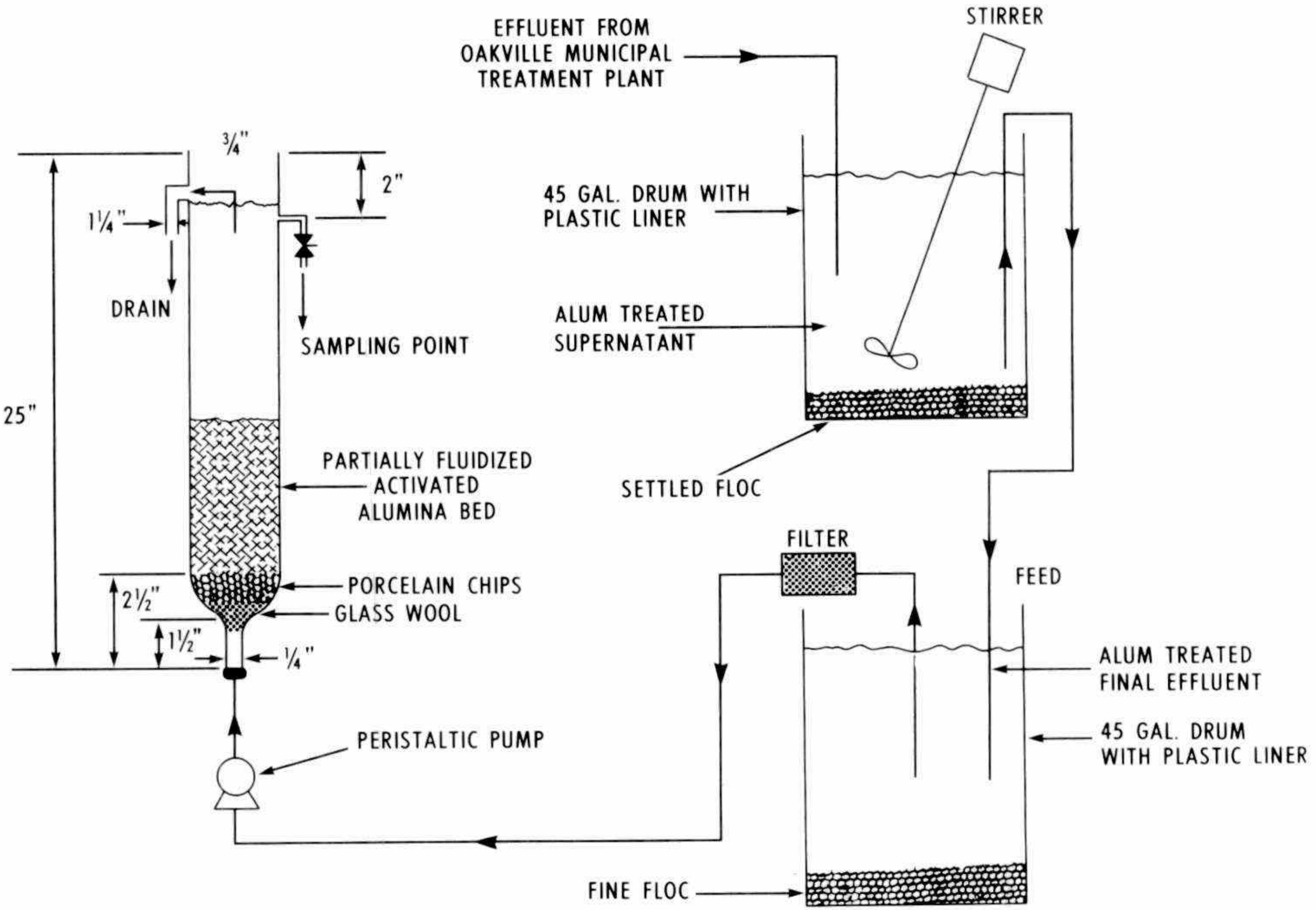
EFFLUENT FROM OAKVILLE MUNICIPAL TREATMENT PLANT
STIRRER
¾"
2"
1¼"
DRAIN
SAMPLING POINT
45 GAL. DRUM WITH PLASTIC LINER
ALUM TREATED SUPERNATANT
25"
SETTLED FLOC
PARTIALLY FLUIDIZED ACTIVATED ALUMINA BED
PORCELAIN CHIPS
GLASS WOOL
2½"
1½"
¼"
FILTER
FEED
ALUM TREATED FINAL EFFLUENT
PERISTALTIC PUMP
45 GAL. DRUM WITH PLASTIC LINER
FINE FLOC

Figure 1 Schematic Diagram of Apparatus

(± 0.03 mg P/l). Analyses of twenty-two effluent samples showed that the average orthophosphate was about one-half of one percent lower than the total average phosphates, as determined by acid digestion prior to the orthophosphate analyses. Furthermore, the use of orthophosphate analyses provided a rapid feedback of information on the column operation because the boiling step in the analytical procedure was omitted.

### 4.3 Regeneration

For the first regeneration of the four columns, 35 bed volumes of either 1N or 2N sodium hydroxide was used in upward flow at a flowrate of 0.6 litres per hour. For the two subsequent regenerations, the 35 bed volumes of caustic were recycled once (i.e., each column was eluted twice, using the same solution). The columns were rinsed with 30 bed volumes of water. Finally, they were rinsed with tap water at a flowrate of 1.2 l/hr until less than 0.1 mg P/l was detected. A fresh glass wool stopper was placed at the base of the columns, and the latter reassembled. To obtain a mass balance, the caustic solutions and rinse waters were analyzed for total phosphorus and aluminum. Total phosphorus analyses were required because activated alumina preferentially adsorbs condensed phosphorus (10); the difference between the total and orthophosphates in the caustic solutions was approximately 13 percent.

# 5. RESULTS AND DISCUSSION

## 5.1 Phase 1

### 5.1.1 Alum pretreatment

Throughout the entire study, the effectiveness of alum treatment on the Oakville Municipal Treatment Plant effluent was evaluated; these results are illustrated in Figure 2 (Phosphorus Residual of Supernatant) and Figure 3 (Suspended Solids). From these probability curves, the data for 80% probability were extracted and are shown in Figure 4. The phosphorus residual curve in Figure 4 shows that an alum treatment of 6 mg/l as Al effectively reduced the phosphorus residual to about 1 mg/l. The results obtained by the personnel of the Oakville Water Pollution Control Plant were similar (Figure 5) but the level of alum dosage required was somewhat greater.

The required alum dosage is significantly increased when phosphorus residuals below 0.5 mg/l are sought. At the highest dosage tested (15 mg/l Al) the phosphorus residual is 0.3 mg/l (Figure 4) and the suspended solids have increased 6.6 times; furthermore, the phosphorus residual curve tends to approach the x-axis asymptotically whereas the suspended solids curve is rising steadily. Thus, further increases in the alum dosage are not economically attractive. The suspended solids data from Figure 4 were utilized to estimate the amount of sludge that would be generated by alum treatment in the economic analyses (Section 5.2.2).

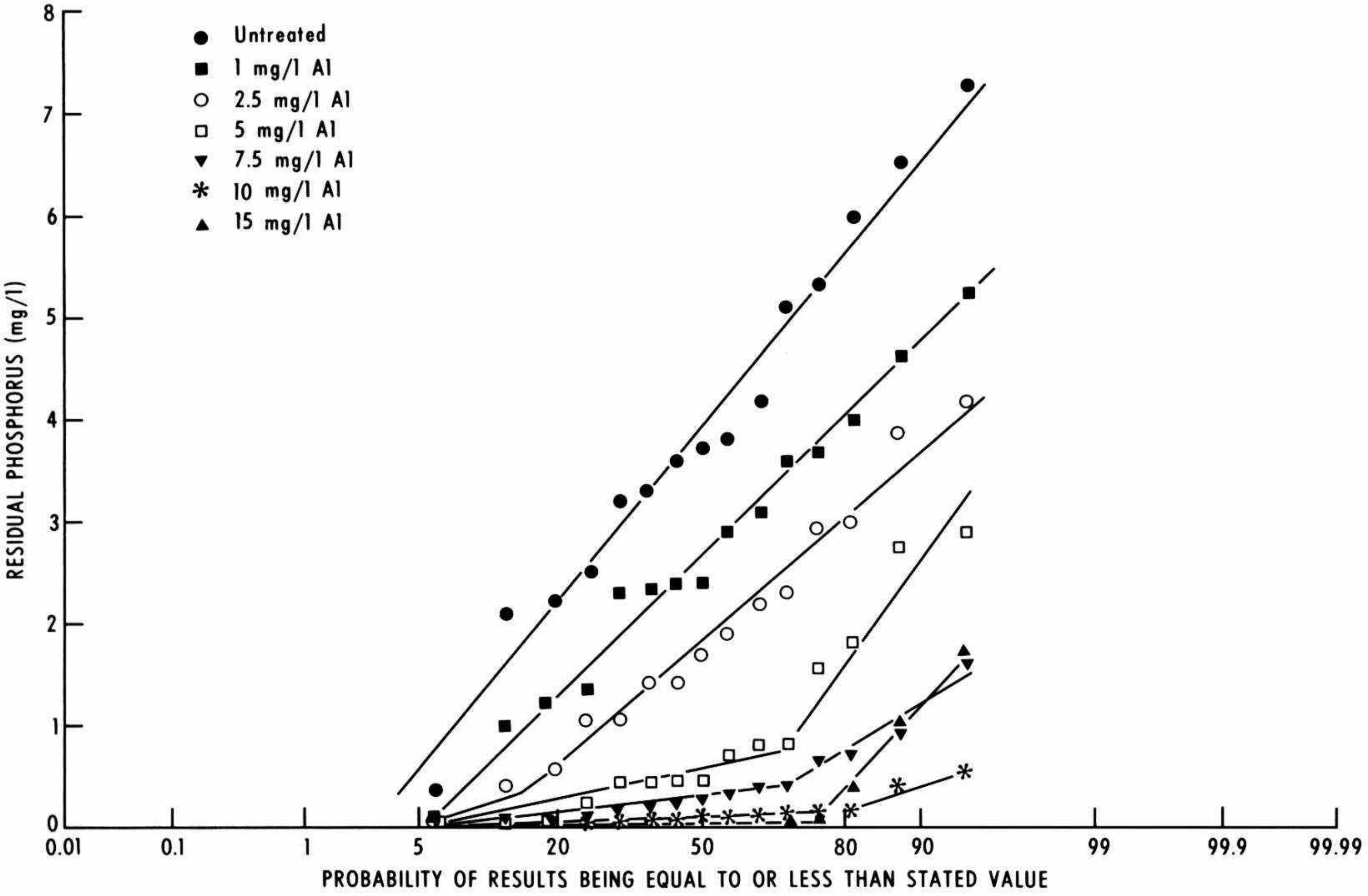

Figure 2 Residual Phosphorus after Treatment of Final Effluent with Alum

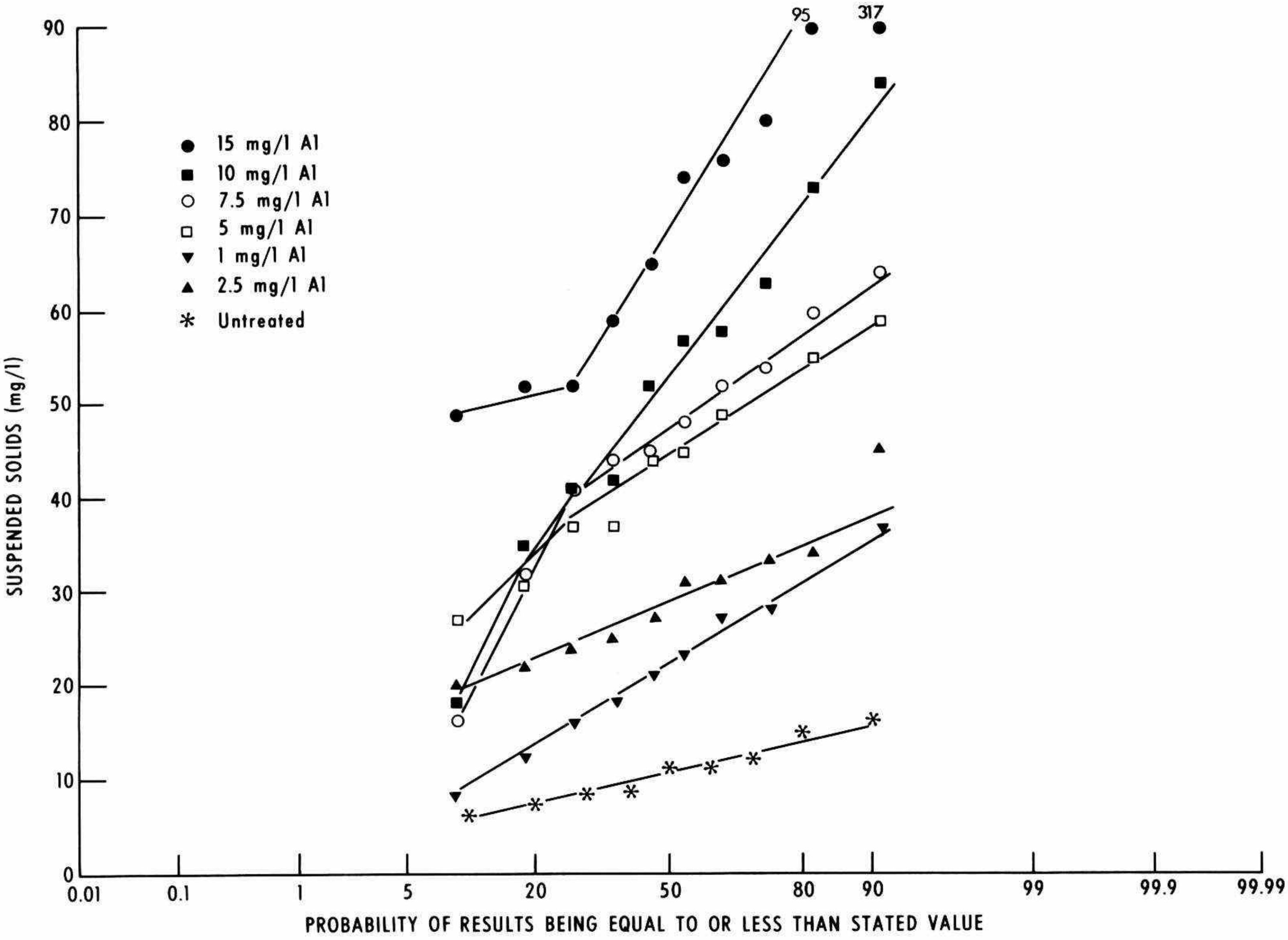

Figure 3 Suspended Solids following Alum Addition to Final Effluent

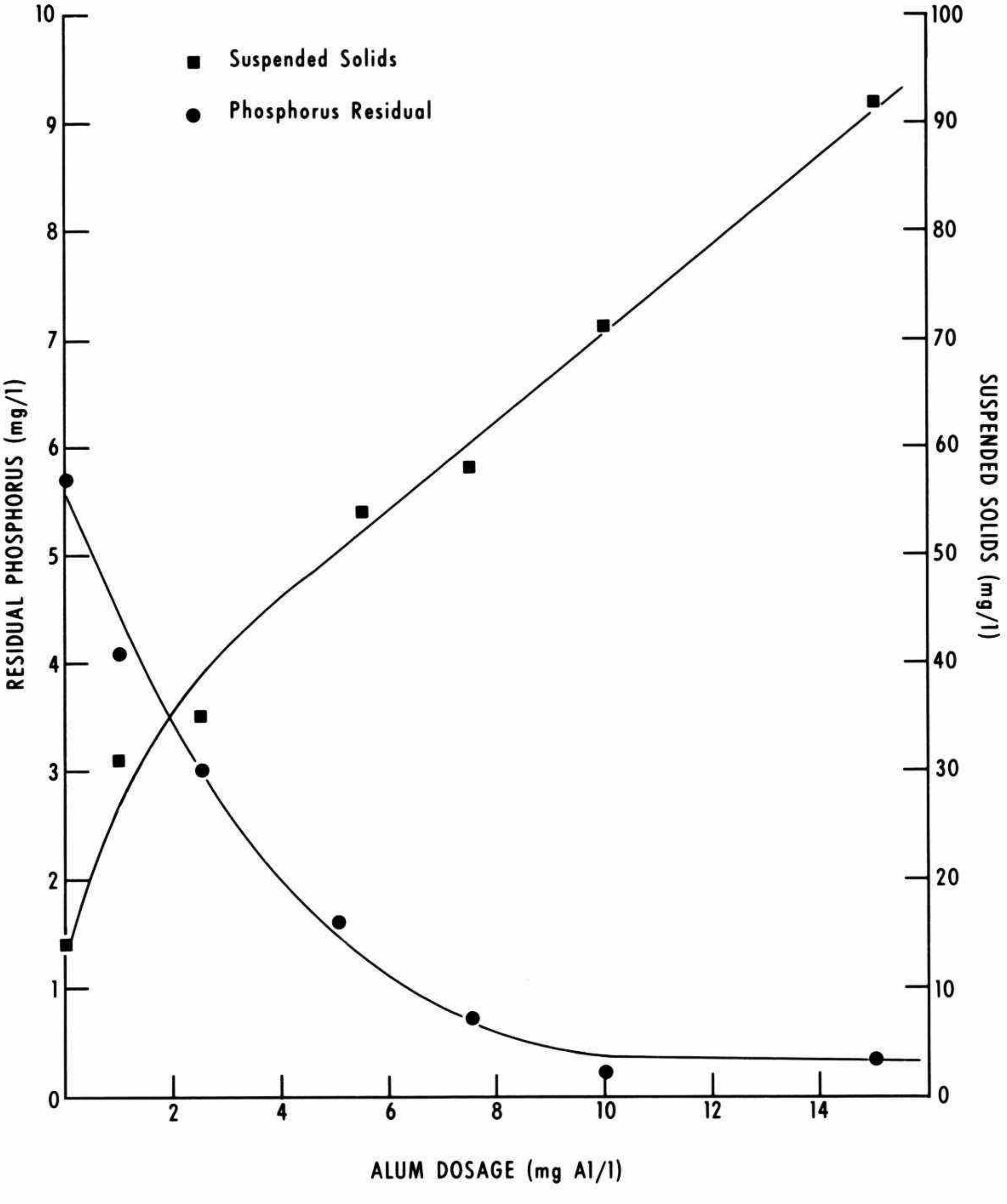

Figure 4 Effect of Alum Treatment on Residual Phosphorus and Suspended Solids Concentrations-80% Probability

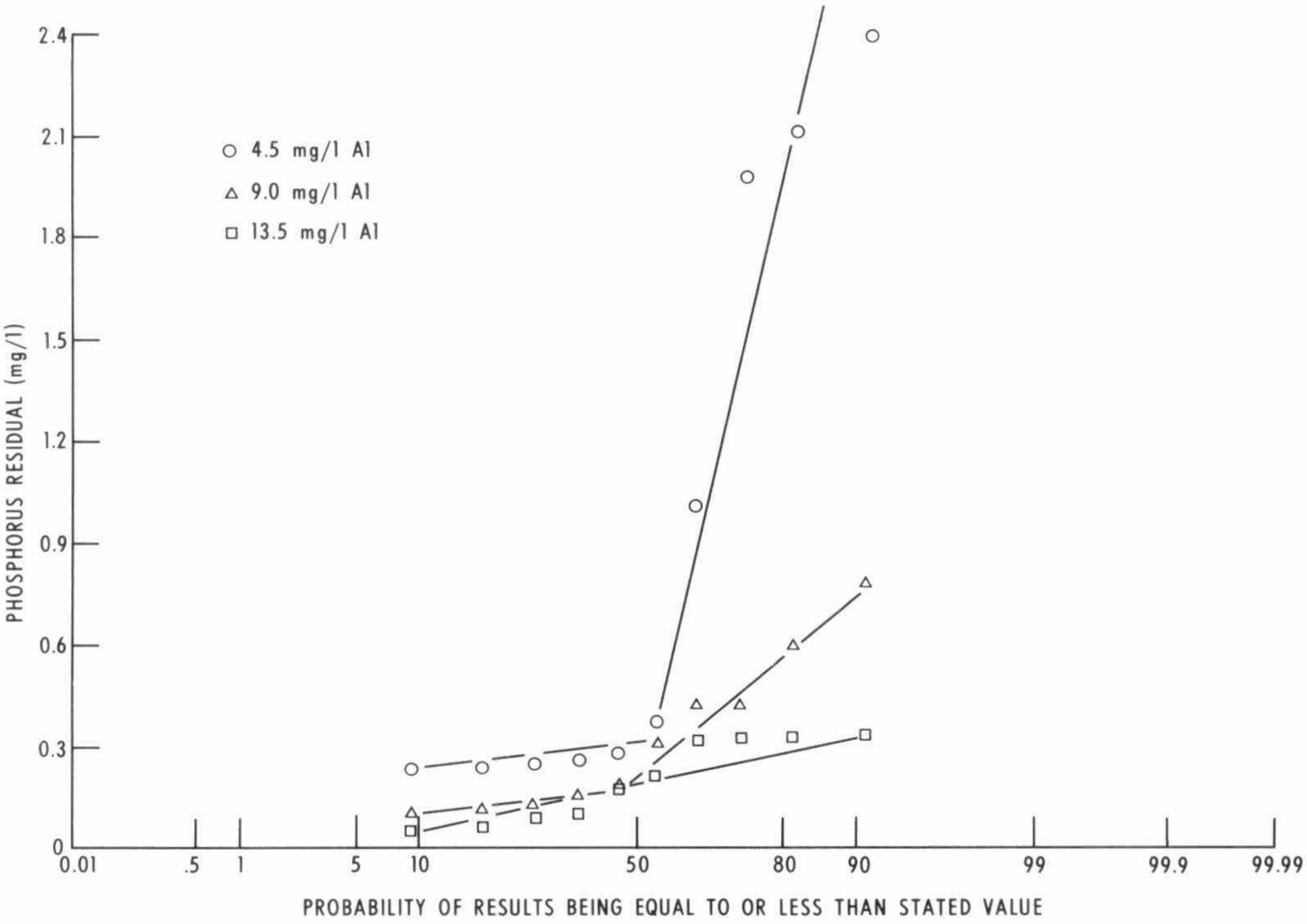

Figure 5 Residual Phosphorus after Treatment of Final Effluent with Alum

### 5.1.2 Operation and regeneration of activated alumina columns

To evaluate sodium hydroxide as a regenerant for exhausted activated alumina, four partially fluidized columns were operated at a constant upflow rate (1.2 l/hr), a constant weight of activated alumina, (30 gm) and two phosphorus influent concentrations, (1 mg/l and 2 mg/l).

These columns were loaded three times with the regeneration step between runs, and the data are summarized in Tables 1 - 6 and Figures 6 - 10. Actually, these data were accumulated twice, but so many difficulties were encountered during the original sequence that the data were discarded.

The initial runs of the four columns were conducted on "fresh" alumina. Two of the columns used alumina that had been activated by water and two columns were activated with 1N nitric acid. Tables 1 and 2 contain the data for runs with designed influent phosphorus concentrations of 1 and 2 mg/l, respectively. Two columns at each concentration were operated, and thus an opportunity to evaluate the need for nitric acid activation was provided. It is evident that washing with nitric acid had little effect in improving the performance of the columns (see Figures 6 and 7).

For this series, the influent phosphorus concentrations were designed on the analyses of filtered feed samples as it was believed that the long settling time (2 days) and glass wool filter would eliminate floc and solids carryover. During the course of the run, it was discovered that the phosphorus analyses of mixed feed samples markedly differed from the filtered values (Table 1) and that the phosphorus concentration in the polished effluent is dependent on the phosphorus concentration of mixed influent.

TABLE 1. PERFORMANCE OF ACTIVATED ALUMINA COLUMNS AT DESIGNED FLOW OF 1.2 l/hr AND DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS AT 1 mg/l.

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | | | PHOSPHORUS BREAKTHROUGH IN EFFLUENT (PERCENT) § | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Day | Hour | (hr) | Unit #1* | | Unit #2** | | Feed Concentration | | Effluent Concentration | | | |
| | | | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | In Mixed Sample | In Filtered Sample | Unit #1 | Unit #2 | Unit #1 | Unit #2 |
| 1 | 4 pm | 0 | 1.26 | 0 | 1.20 | 0 | 1.00 | 1.00 | 0 | 0 | 0 | 0 |
| 1 | 11 pm | 7 | 1.26 | 270 | 1.20 | 260 | | | 0.03 | 0.03 | 3 | 3 |
| 2 | 12 am | 20 | 1.26 | 760 | 1.20 | 730 | | | 0.06 | 0.06 | 6 | 6 |
| 2 | 10 pm | 30 | 1.20 | 1,100 | 1.32 | 1,100 | | | 0.06 | 0.07 | 6 | 7 |
| 3 | 12 am | 44 | 1.11 | 1,600 | 1.26 | 1,700 | | | 0.10 | 0.14 | 10 | 11 |
| 3 | 2 pm | 46 | 1.08 | 1,700 | 1.32 | 1,700 | 1.26 | 1.00 | - | - | - | - |
| 3 | 10 pm | 54 | 1.08 | 2,000 | 1.32 | 2,100 | | | 0.10 | 0.19 | 8 | 15 |
| 4 | 9 am | 65 | 0.60 Y | 2,200 | 1.32 Y | 2,400 | | | 0.14 | 0.23 | 11 | 18 |
| 4 | 12 am | 68 | 1.14 | 2,300 | 1.32 | 2,500 | | | 0.15 | 0.23 | 12 | 18 |
| 4 | 3 pm | 71 | 1.14 | 2,400 | 1.32 | 2,700 | | | 0.15 | 0.23 | 12 | 18 |
| 4 | 9 pm | 77 | 1.14 | 2,600 | 1.32 | 2,900 | 1.84 | 1.12 | 0.21 | 0.33 | 17 | 26 |
| 5 | 9 am | 89 | 0.78 Y | 3,000 | 1.14 Y | 3,300 | | | 0.57 | 0.65 | 31 | 35 |
| 5 | 12 am | 92 | 1.14 Y | 3,100 | 1.17 Y | 3,400 | | | 0.68 | 0.76 | 37 | 41 |

* Weight of Alumina - Unit #1 - 30.34 gm, $HNO_3$ washed

** Weight of Alumina - Unit #2 - 28.25 gm, $H_2O$ washed

§ Calculations based on phosphorus concentration in mixed sample

Y Flow rates adjusted to 1.2 l/hr

TABLE 1. (CONT'D)

Designed Flow - 1.2 l/hr

Designed Influent Concentration of Phosphorus - 1 mg/l

| SAMPLING TIME | | LENGTH OF RUN (hr) | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | | | PHOSPHORUS BREAKTHROUGH IN EFFLUENT (PERCENT) § | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Day | Hour | | Unit #1* | | Unit #2** | | Feed Concentration | | Effluent Concentration | | Unit #1 | Unit #2 |
| | | | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | In Mixed Sample | In Filtered Sample | Unit #1 | Unit #2 | | |
| 5 | 4 pm | 96 | 1.02 | 3,200 | 1.20 | 3,600 | 1.84 | 1.12 | 0.66 | 0.75 | 36 | 41 |
| 5 | 11 pm | 103 | 1.14 | 3,400 | 1.20 | 3,800 | | | 0.67 | 0.77 | 36 | 42 |
| 6 | 9 am | 113 | 0.96 Y | 3,800 | 1.14 Y | 4.200 | | | 0.70 | 0.77 | 38 | 42 |
| 6 | 1 pm | 117 | 1.20 | 3,900 | 1.38 | 4,400 | 1.56 | 1.02 | 0.71 | 0.79 | 39 | 43 |
| 6 | 4 pm | 120 | 1.20 | 4,000 | 1.32 | 4,500 | | | 0.57 | 0.67 | 37 | 43 |
| 6 | 12 pm | 128 | 0.90 Y | 4,300 | 0.90 Y | 4,700 | | | 0.51 | 0.62 | 33 | 40 |
| 7 | 9 am | 137 | 1.02 | 4,500 | 1.26 | 5,000 | | | 0.66 | 0.70 | 42 | 45 |
| 7 | 4 pm | 144 | 1.02 | 4,700 | 1.26 | 5,300 | | | 0.56 | 0.62 | 36 | 40 |
| 7 | 10 pm | 150 | 1.02 | 4,800 | 1.26 | 5,500 | 1.28 | - | 0.56 | 0.64 | 36 | 41 |
| 8 | 9 am | 161 | 1.02 | 5,300 | 1.26 | 6,000 | | | 0.50 | 0.67 | 39 | 52 |

* Weight of Alumina - Unit #1 - 30.34 gm, $HNO_3$ washed

** Weight of Alumina - Unit #2 - 28.25 gm, $H_2O$ washed

§ Calculations based on phosphate concentration in mixed sample

Y Flow rates adjusted to 1.2 l/hr

TABLE 2. PERFORMANCE OF ACTIVATED ALUMINA COLUMNS AT DESIGNED FLOW OF 1.2 l/hr AND DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS AT 2 mg/l.

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION (mg P/l) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed | | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | Mixed Sample | Filtered Sample | Unit #1 | Unit #2 |
| 1 | 4 pm | 0 | 1.20 | 0 | 1.20 | 0 | - | 2.02 | 0 | 0 |
| 1 | 11 pm | 7 | 1.20 | 260 | 1.20 | 260 | | | 0.10 | 0.09 |
| 2 | 12 am | 20 | 1.20 | 730 | 1.20 | 730 | | | 0.13 | 0.12 |
| 2 | 10 pm | 30 | 1.20 | 1100 | 1.20 | 1100 | | | 0.19 | 0.15 |
| 3 | 12 am | 44 | 1.14 | 1600 | 1.20 | 1600 | | | 0.29 | 0.29 |
| 3 | 2 pm | 46 | 1.14 | 1700 | 1.20 | 1700 | 2.24 | 1.91 | - | - |
| 3 | 10 pm | 54 | $0.90^{+}$ | 1900 | $1.38^{+}$ | 2000 | | | 0.43 | 0.46 |
| 4 | 9 am | 65 | 1.08 | 2300 | 1.20 | 2400 | | | 0.68 | 0.67 |
| 4 | 12 am | 68 | 1.14 | 2400 | 1.20 | 2500 | | | 0.71 | 0.71 |
| 4 | 3 pm | 71 | 1.14 | 2500 | 1.20 | 2600 | | | 0.71 | 0.74 |
| 4 | 9 pm | 77 | 1.14 | 2700 | 1.20 | 2800 | 1.96 | 1.78 | - | - |
| 5 | 9 am | 89 | $0.72^{+}$ | 3000 | $1.26^{+}$ | 3300 | | | 0.74 | 0.80 |
| 5 | 12 am | 92 | 1.08 | 3100 | 1.26 | 3400 | | | 0.79 | 0.83 |

* Weight of Alumina Unit #1 - 30.30 gm, $HNO_3$ washed

** Weight of Alumina Unit #2 - 29.14 gm, $H_2O$ washed

+ Flow Rates Adjusted to 1.2 l/hr

TABLE 2. (CONT'D)

**Designed Flow - 1.2 l/hr**
**Designed Influent Concentration of Phosphorus - 2 mg/l**

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION (mg P/l) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed | | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | Mixed Sample | Filtered Sample | Unit #1 | Unit #2 |
| 5 | 4 pm | 96 | $0.90^{+}$ | 3200 | $1.26^{+}$ | 3500 | 1.96 | 1.78 | 0.79 | 0.83 |
| 5 | 11 pm | 103 | 1.14 | 3500 | 1.32 | 3800 | | | 0.79 | 0.94 |
| 6 | 9 am | 113 | 0.96 | 3800 | 1.32 | 4200 | | | 0.90 | 1.07 |
| 6 | 1 pm | 117 | 1.20 | 3900 | 1.32 | 4400 | 2.10 | 1.90 | 0.90 | 1.12 |
| 6 | 4 pm | 120 | 1.14 | 4000 | 1.32 | 4500 | | | 1.03 | 1.26 |
| 6 | 12 pm | 128 | $0.90^{+}$ | 4300 | $0.90^{+}$ | 4800 | | | 1.08 | 1.24 |
| 7 | 9 am | 137 | 1.02 | 4700 | 1.26 | 5100 | | | 1.14 | 1.38 |
| 7 | 4 pm | 144 | 1.02 | 4900 | 1.26 | 5400 | | | 1.18 | 1.40 |
| 7 | 10 pm | 150 | 1.02 | 5100 | 1.26 | 5600 | 1.87 | - | 1.24 | 1.42 |
| 8 | 9 am | 161 | 1.02 | 5400 | 1.26 | 6000 | | | 1.28 | 1.41 |

* Weight of Alumina Unit #1 - 30.30 gm, $HNO_3$ washed
** Weight of Alumina Unit #2 - 29.14 gm, $H_2O$ washed
+ Flow rates adjusted to 1.2 l/hr

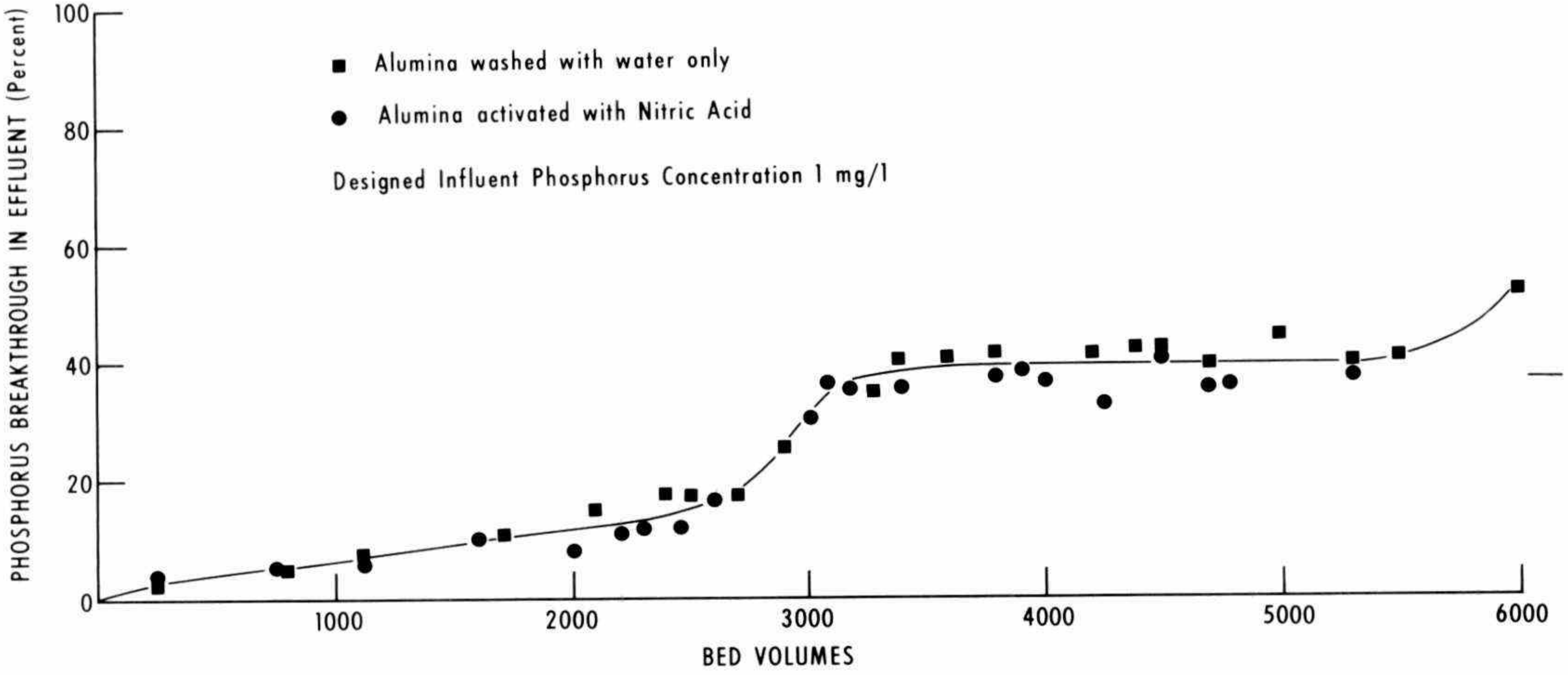

Figure 6 Effect of Nitric Acid Activation on Column Performance

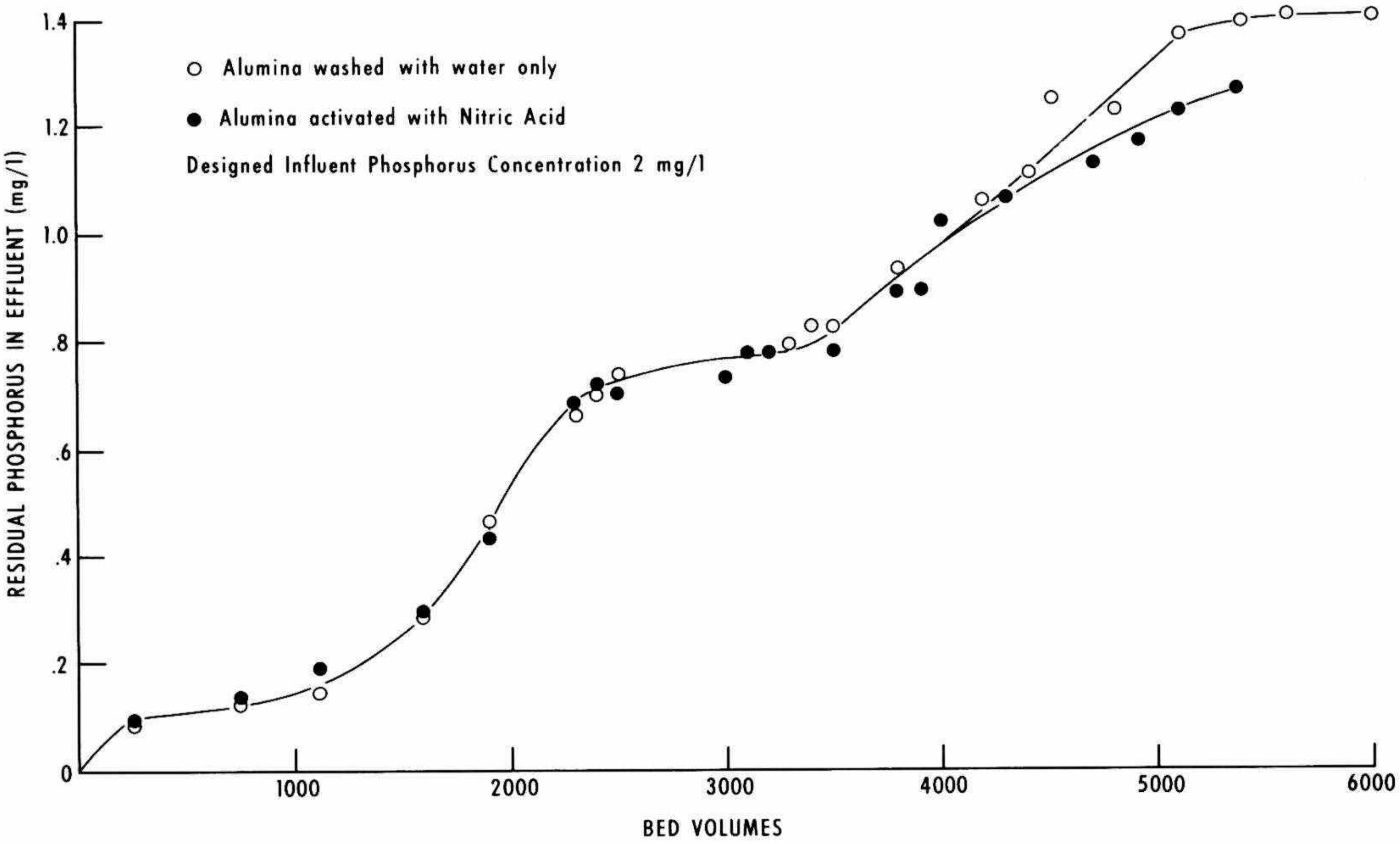

Figure 7 Effect of Nitric Acid Activation on Column Performance

The results of the initial run (Table 1) are expressed in terms of the residual concentration as well as the percentage of phosphorus breakthrough. Calculation of the breakthrough is based on the phosphorus concentration in the mixed sample of influent (weighted average 1.33 mg/l).

The columns were regenerated with 35 bed volumes of 1N and 2N sodium hydroxide. After the second and third runs, the regenerant was recycled once. The data for these runs are summarized in Tables 3 and 5 for the influent phosphorus concentration of 1 mg/l and Tables 4 and 6 for the corresponding influent concentration of 2 mg/l; Figures 8, 9 and 10 illustrate the data and the initial curves obtained with "fresh" alumina were included for comparative purposes.

When the influent phosphorus concentration was 1 mg/l the data (Tables 3 and 5) showed that regeneration by 1N NaOH was just as effective as 2N NaOH. In Figure 8, the data obtained for columns regenerated with 1N NaOH are shown while the corresponding data for 2N NaOH are only reported in Table 4. In general, Figure 8 indicates that the performance of regenerated alumina is comparable to that observed originally. The plateaus for the two runs following regeneration occurred at slightly different phosphorus levels (0.45 and 0.30 mg/l) but the initial and final portions of the curves are the same within the experimental error. The lower plateau was obtained when the alumina was regenerated with 1N NaOH recycled once. The plateau for the column with "fresh" alumina lies between the two plateaus for regenerated alumina. This was due to the fact that the average influent phosphorus concentration was 1.3 mg/l for the run with the fresh alumina rather than 1.0 mg P/l as in the other two cases. The differences, however, are so slight (approximately .15 mg P/l) that it was concluded that this regeneration procedure effectively restored the capacity of the activated alumina.

TABLE 3. PERFORMANCE OF COLUMNS FOLLOWING FIRST REGENERATION AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS IN MIXED SAMPLE OF 1 mg/l.

Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes Ƶ | Rate (l/hr) | Bed Volumes Ƶ | | Unit #1 | Unit #2 |
| 1 | 10 am | 0 | 1.2 | 0 | 1.2 | 0 | 0.81 | 0 | 0 |
| 1 | 4 pm | 4 | 1.2 | 150 | 1.2 | 150 | | 0.02 | 0.02 |
| 1 | 5 pm | 7 | 1.2 | 250 | 1.2 | 250 | | 0.02 | 0.03 |
| 1 | 11 pm | 13 | 1.3 | 470 | 1.2 | 470 | | 0.02 | 0.03 |
| 2 | 9 am | 23 | 1.3 | 840 | 1.2 | 840 | | 0.04 | 0.06 |
| 2 | 2 pm | 28 | - | 1000 | - | 1000 | 1.08 | 0.06 | 0.08 |
| 2 | 5 pm | 31 | 1.2 | 1100 | 1.2 | 1100 | | 0.08 | 0.14 |
| 2 | 11 pm | 37 | 1.2 | 1300 | 1.2 | 1300 | | 0.08 | 0.17 |
| 3 | 9 am | 47 | 1.2 | 1700 | 1.2 | 1700 | | 0.16 | 0.21 |
| 3 | 5 pm | 55 | 1.3 | 2000 | 1.0 | 2000 | | 0.23 | 0.23 |
| 3 | 11 pm | 61 | 1.2 | 2200 | 1.2 | 2200 | | 0.20 | 0.20 |
| 4 | 9 am | 71 | 1.2 | 2600 | 1.2 | 2600 | | 0.25 | 0.21 |
| 4 | 1 pm | 75 | 1.2 | 2700 | 1.2 | 2700 | | 0.30 | 0.25 |

* Weight of Alumina Unit #1 - 30.34 gm
** Weight of Alumina Unit #2 - 28.25 gm
Y Flow Rates adjusted to 1.2 l/hr
Ƶ Bed Volumes calculated assuming average flows of 1.2 l/hr for 196 hours; 1.0 l/hr for next 49 hours; 0.7 l/hr for 44 hours; and 0.35 l/hr for final 20 hours.

TABLE 3. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes Ƶ | Rate (l/hr) | Bed Volumes Ƶ | | Unit #1 | Unit #2 |
| 4 | 5 pm | 79 | 1.2 | 2900 | 1.2 | 2900 | 1.08 | 0.33 | 0.25 |
| 4 | 10 pm | 84 | 1.3 | 3100 | 1.2 | 3100 | | 0.39 | 0.29 |
| 5 | 11 am | 95 | 1.3 Y | 3500 | 0.9 Y | 3500 | 1.05 | 0.46 | 0.43 |
| 5 | 7 pm | 103 | 1.4 Y | 3700 | 1.3 Y | 3700 | | 0.36 | 0.34 |
| 6 | 2 pm | 122 | 1.3 | 4400 | 1.2 | 4400 | | 0.44 | 0.46 |
| 6 | 11 pm | 131 | 1.3 | 4800 | 1.2 | 4800 | | 0.44 | 0.46 |
| 7 | 9 am | 141 | 1.2 | 5100 | 1.2 | 5100 | | 0.45 | 0.47 |
| 7 | 2 pm | 146 | - | 5300 | - | 5300 | 1.03 | 0.45 | 0.47 |
| 7 | 4 pm | - | 1.2 | | 1.2 | | | | |
| 7 | 5 pm | 149 | 1.2 | 5400 | 1.2 | 5400 | | 0.43 | 0.57 |
| 7 | 10 pm | 154 | 1.4 Y | 5600 | 1.2 Y | 5600 | | 0.46 | 0.57 |
| 8 | 9 am | 165 | 0.9 Y | 6000 | 1.1 Y | 6000 | | 0.45 | 0.52 |

* Weight of Alumina Unit #1 - 30.34 gm
** Weight of Alumina Unit #2 - 28.25 gm
Y Flow Rates adjusted to 1.2 l/hr
Ƶ Bed Volumes calculated assuming average flows of 1.2 l/hr for 196 hours; 1.0 l/hr for next 49 hours; 0.7 l/hr for 44 hours;and 0.35 l/hr for final 20 hours.

TABLE 3. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | | Unit #1 | Unit #2 |
| 8 | 2 pm | 170 | 1.0[Y] | 6200 | 1.1[Y] | 6200 | 1.03 | 0.45 | 0.52 |
| 8 | 5 pm | 173 | 1.2 | 6300 | 1.2 | 6300 | | 0.42 | 0.48 |
| 9 | 9 am | 189 | 1.0 | 6900 | 1.2 | 6900 | | 0.48 | 0.52 |
| 9 | 4 pm | 196 | 1.0 | 7100 | 1.2 | 7100 | 1.00 | 0.46 | 0.54 |
| 10 | 9 am | 213 | 1.0[Y] | 7600 | 1.1[Y] | 7600 | | 0.60 | 0.62 |
| 10 | 1 pm | 217 | 1.0[Y] | 7700 | 1.1[Y] | 7800 | | 0.59 | 0.64 |
| 11 | 9 am | 237 | 0.8[Y] | 8300 | 0.9[Y] | 8300 | | 0.66 | 0.64 |
| 11 | 1 pm | 241 | 1.1[Y] | 8500 | 1.1[Y] | 8500 | | 0.70 | 0.66 |
| 11 | 5 pm | 245 | 1.1 | 8600 | 1.2 | 8600 | 1.10 | 0.66 | 0.66 |
| 13 | 1 pm | 289 | 0.6[Y] | 9500 | 0.8[Y] | 9500 | | 0.73 | 0.75 |
| 14 | 9 am | 309 | 0.3 | 9700 | 0.4 | 9700 | 1.13 | 0.71 | 0.72 |

* Weight of Alumina Unit #1 - 30.34 gm
** Weight of Alumina Unit #2 - 28.25 gm
Y Flow Rates adjusted to 1.2 l/hr
Ƶ Bed Volumes calculated assuming average flows of 1.2 l/hr for 196 hr; 1.0 l/hr for next 49 hours. 0.7 l/hr for 44 hr; and 0.35 l/hr for final 20 hours.

TABLE 4. PERFORMANCE OF COLUMNS FOLLOWING FIRST REGENERATION AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS IN MIXED SAMPLE OF 2 mg/l.

Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | | Unit #1 | Unit #2 |
| 1 | 10 am | 0 | 1.2 | 0 | 1.2 | 0 | 1.95 | 0 | 0 |
| 1 | 2 pm | 4 | 1.2 | 150 | 1.2 | 150 | | 0.12 | 0.12 |
| 1 | 5 pm | 7 | 1.2 | 250 | 1.2 | 250 | | 0.14 | 0.12 |
| 1 | 11 pm | 13 | 1.2 | 470 | 1.2 | 470 | | 0.32 | 0.23 |
| 2 | 9 am | 23 | 1.2 | 840 | 1.2 | 840 | | 0.37 | 0.20 |
| 2 | 2 pm | 28 | 1.2 | 1000 | 1.2 | 1000 | | 0.40 | 0.20 |
| 2 | 5 pm | 31 | 1.2 | 1100 | 1.2 | 1100 | | 0.36 | 0.18 |
| 2 | 11 pm | 37 | 1.2 | 1300 | 1.2 | 1300 | | 0.45 | 0.12 |
| 3 | 9 am | 47 | 1.2 | 1700 | 1.2 | 1700 | | 0.57 | 0.39 |
| 3 | 2 pm | 52 | 1.2 | 1900 | 1.2 | 1900 | 1.98 | 0.76 | 0.58 |
| 3 | 5 pm | 55 | 1.3 | 2000 | 1.3 | 2000 | | 0.73 | 0.52 |
| 3 | 11 pm | 61 | 1.2 | 2200 | 1.2 | 2200 | | 0.87 | 0.75 |
| 4 | 9 am | 71 | 1.2 | 2600 | 1.2 | 2600 | | 1.00 | 0.94 |

* Weight of Alumina Unit #1 - 30.30 gm
** Weight of Alumina Unit #2 - 29.14 gm
+ Flow Rate Adjusted to 1.2 l/hr

TABLE 4. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 2 mg/l
Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | | Unit #1 | Unit #2 |
| 4 | 1 pm | 75 | 1.2 | 2700 | 1.2 | 2700 | 1.98 | 1.06 | 1.02 |
| 4 | 5 pm | 79 | 1.2 | 2900 | 1.2 | 2900 | | 1.10 | 1.12 |
| 4 | 10 pm | 84 | 0.6+ | 3100 | 1.2 | 3100 | | 1.10 | 1.18 |
| 5 | 11 am | 95 | 1.2 | 3500 | 1.3 | 3500 | | 1.36 | 1.46 |
| 5 | 7 pm | 103 | 1.1 | 3700 | 1.3 | 3700 | | 1.30 | 1.41 |

* Weight of Alumina Unit #1 - 30.30 gm
** Weight of Alumina Unit #2 - 29.14 gm
+ Flow Rate Adjusted to 1.2 l/hr

TABLE 5. PERFORMANCE OF COLUMNS FOLLOWING SECOND REGENERATION AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS IN MIXED SAMPLE OF 1 mg/l.

**Designed Flow - 1.2 l/hr**
**Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH, Recycled Once**
**Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH, Recycled Once**

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (1/hr) | Bed Volumes | Rate (1/hr) | Bed Volumes | | Unit #1 | Unit #2 |
| 1 | 12 am | 0 | 1.2 | 0 | 1.2 | 0 | 1.00 | 0 | 0 |
| 1 | 5 pm | 5 | 1.2 | 180 | 1.2 | 180 | | 0.03 | 0.04 |
| 1 | 11 pm | 11 | 1.2 | 400 | 1.2 | 400 | | 0.04 | 0.08 |
| 2 | 1 pm | 25 | 1.2 | 900 | 1.2 | 900 | | 0.03 | 0.11 |
| 3 | 1 am | 37 | 1.2 | 1300 | 1.2 | 1300 | | 0.08 | 0.14 |
| 3 | 12 am | 48 | 1.2 | 1700 | 1.2 | 1700 | | 0.13 | 0.16 |
| 3 | 11 pm | 59 | 1.2 | 2100 | 1.2 | 2100 | | 0.15 | 0.32 |
| 4 | 9 am | 69 | 1.2 | 2500 | 1.2 | 2500 | 0.90 | 0.22 | 0.29 |
| 4 | 2 pm | 74 | 1.2 | 2700 | 1.2 | 2700 | | 0.25 | 0.25 |
| 4 | 5 pm | 77 | 1.2 | 2800 | 1.2 | 2800 | | 0.27 | 0.27 |
| 5 | 9 am | 93 | 1.2 | 3400 | 1.2 | 3400 | | - | - |
| 5 | 12 am | 96 | 1.2 | 3500 | 1.2 | 3500 | | - | - |
| 5 | 5 pm | 101 | 1.2 | 3700 | 1.2 | 3700 | | - | 0.32 |

* Weight of Alumina Unit #1 - 30.34 gm

** Weight of Alumina Unit #2 - 28.25 gm

TABLE 5. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH, Recycled Once
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH, Recycled Once

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | | Unit #1 | Unit #2 |
| 5 | 12 pm | 108 | 1.2 | 3900 | 1.2 | 3900 | 0.90 | 0.24 | 0.31 |
| 6 | 9 am | 117 | 1.2 | 4300 | 1.3 | 4300 | | 0.27 | 0.35 |
| 6 | 12 am | 120 | 1.2 | 4400 | 1.3 | 4400 | | 0.28 | 0.35 |
| 6 | 4 pm | 124 | 1.2 | 4500 | 1.3 | 4500 | | 0.32 | 0.40 |
| 6 | 11 pm | 131 | 1.2 | 4800 | 1.3 | 4800 | 1.07 | 0.32 | 0.38 |
| 7 | 9 am | 141 | 1.3 | 5100 | 1.3 | 5100 | | 0.30 | 0.30 |
| 7 | 2 pm | 146 | 1.2 | 5300 | 1.3 | 5300 | | 0.33 | 0.30 |
| 7 | 5 pm | 149 | 1.2 | 5400 | 1.2 | 5400 | | 0.31 | 0.32 |
| 8 | 9 am | 165 | 1.2 | 6000 | 1.2 | 6000 | | 0.40 | 0.38 |
| 8 | 1 pm | 169 | 1.3 | 6100 | 1.2 | 6100 | | 0.46 | 0.48 |
| 9 | 11 am | 191 | 1.3 | 6900 | 1.2 | 6900 | | 0.52 | 0.54 |

* Weight of Alumina Unit #1 - 30.34 gm

** Weight of Alumina Unit #2 - 28.25 gm

TABLE 5. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH, Recycled Once
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH, Recycled Once

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | | Unit #1 | Unit #2 |
| 9 | 5 pm | 197 | 1.2 | 7200 | 1.2 | 7200 | 1.22 | 0.54 | 0.54 |
| 10 | 9 pm | 225 | 1.1 | 8200 | 1.1 | 8200 | | 0.60 | 0.62 |
| 11 | 11 am | 239 | 1.1 | 8700 | 1.1 | 8700 | | 0.66 | 0.67 |
| 11 | 9 pm | 249 | 1.1 | 9100 | 1.1 | 9100 | | 0.71 | 0.76 |

* Weight of Alumina Unit #1 - 30.34 gm
** Weight of Alumina Unit #2 - 28.25 gm

TABLE 6. PERFORMANCE OF COLUMNS FOLLOWING SECOND REGENERATION AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS IN MIXED SAMPLE OF 2 mg/l.

Designed Flow - 1.2 l/hr
Unit #1 - Regenerated With 35 Bed Volumes of 1N NaOH, Recycled Once
Unit #2 - Regenerated With 35 Bed Volumes of 2N NaOH, Recycled Once

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | | | ORTHOPHOSPHATE CONCENTRATION mg P/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unit #1* | | Unit #2** | | Feed In Mixed Sample | Effluent | |
| Day | Hour | (Hours) | Rate (l/hr) | Bed Volumes | Rate (l/hr) | Bed Volumes | | Unit #1 | Unit #2 |
| 1 | 12 am | 0 | 1.2 | 0 | 1.2 | 0 | 1.90 | 0 | 0 |
| 1 | 5 pm | 5 | 1.2 | 180 | 1.2 | 180 | | 0.13 | 0.05 |
| 1 | 11 pm | 11 | 1.2 | 400 | 1.2 | 400 | | 0.14 | 0.05 |
| 2 | 4 pm | 19 | 1.2 | 690 | 1.2 | 690 | | - | - |
| | 5 pm | 20 | - | - | 1.2 | 730 | | - | 0.12 |
| 3 | 9 am | 36 | 1.2 | 1300 | 1.2 | 1300 | | 0.59 | 0.48 |
| 3 | 12 am | 39 | 1.3 | 1400 | 1.3 | 1400 | | 0.71 | 0.60 |
| 3 | 5 pm | 44 | 1.3 | 1600 | 1.3 | 1600 | | 0.69 | 0.60 |
| 3 | 12 pm | 51 | 1.3 | 1900 | 1.3 | 1900 | | 0.87 | 0.76 |
| 4 | 9 am | 60 | 1.2 | 2200 | 1.2 | 2200 | | 1.03 | 1.03 |
| 4 | 12 am | 63 | 1.2 | 2300 | 1.2 | 2300 | | 1.06 | 1.06 |
| 4 | 4 pm | 67 | 1.2 | 2400 | 1.2 | 2400 | | 1.13 | 1.08 |

* Weight of Alumina Unit #1 - 30.30 gm

** Weight of Alumina Unit #2 - 29.14 gm

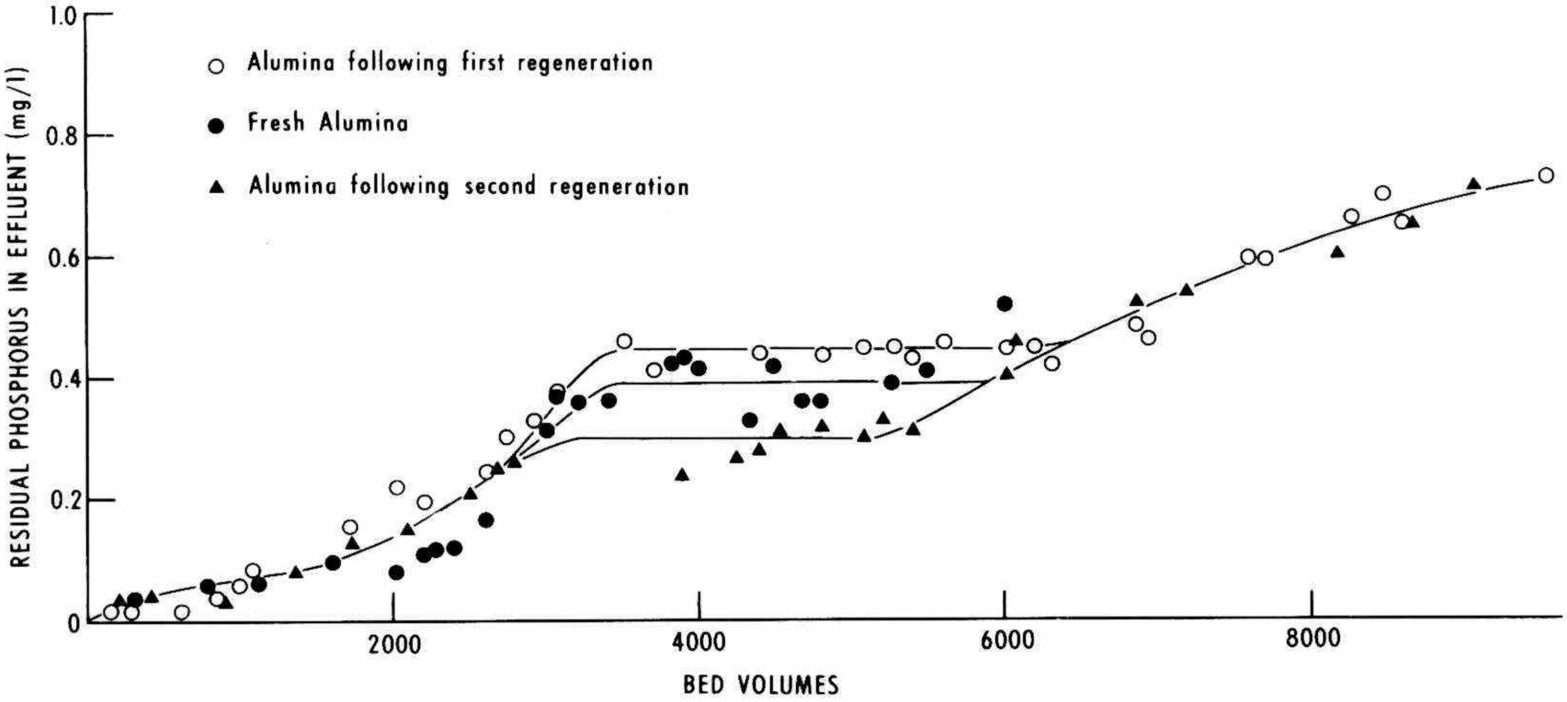

Figure 8 Effect of Regeneration on Activated Alumina Performance

Designed influent phosphorus concentration 1 mg/l

Designed flow 1.2 l/hr

Regenerant- 1N NaOH

An increase in regenerant concentration did not significantly improve regenerant effectiveness. However, the increase in the contact time between regenerant and alumina particles resulted in a slightly lower equilibrium plateau of the third run.

When the influent phosphorus concentration was 2 mg/l, the regeneration of the medium was only partial (Figures 9 and 10). The increase in regenerant concentration improved the effectiveness to some extent but the full performance of the alumina was not restored. Similarly, a slight improvement was noticed during the initial portion of the run when the regenerant of either concentration was recycled.

### 5.1.3 Phosphorus balance

A phosphorus balance was calculated from the column operation and regeneration data (Tables 7, 8). The phosphorus loading was interpolated from measured values of feed phosphorus concentrations and flowrate at each sampling time. The phosphorus leaving the system in the effluent was estimated by numerical integration of the effluent concentration curves. The curve was segmented such that the portion under consideration approximated a straight line; then the areas of the trapezoids produced by verticals to the X-axis were calculated, converted to mg P/l and summed. From these data, the alumina capacity was estimated.

When the concentration of phosphorus in the influent was 1 mg/l, the capacity of the alumina was approximately 6.5 mg P/gm $Al_2O_3$ for all 3 runs which is comparable to that reported by Yee (10), and Ames and Dean (1). However, when 2 mg P/l influent was fed to the columns, this capacity of alumina decreased rapidly after regeneration despite high adsorption in the first run.

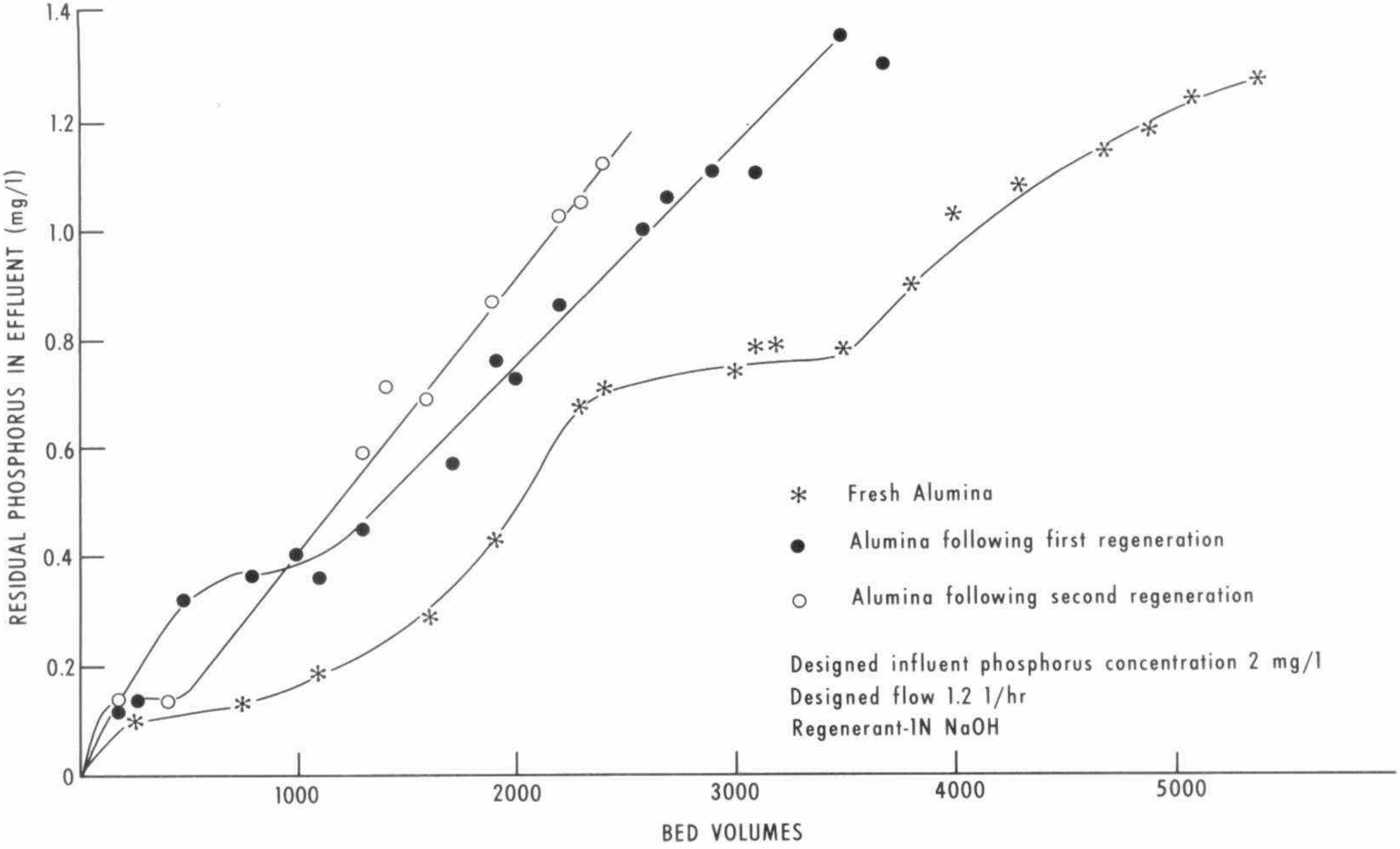

Figure 9 Effect of Regeneration on Activated Alumina Performance

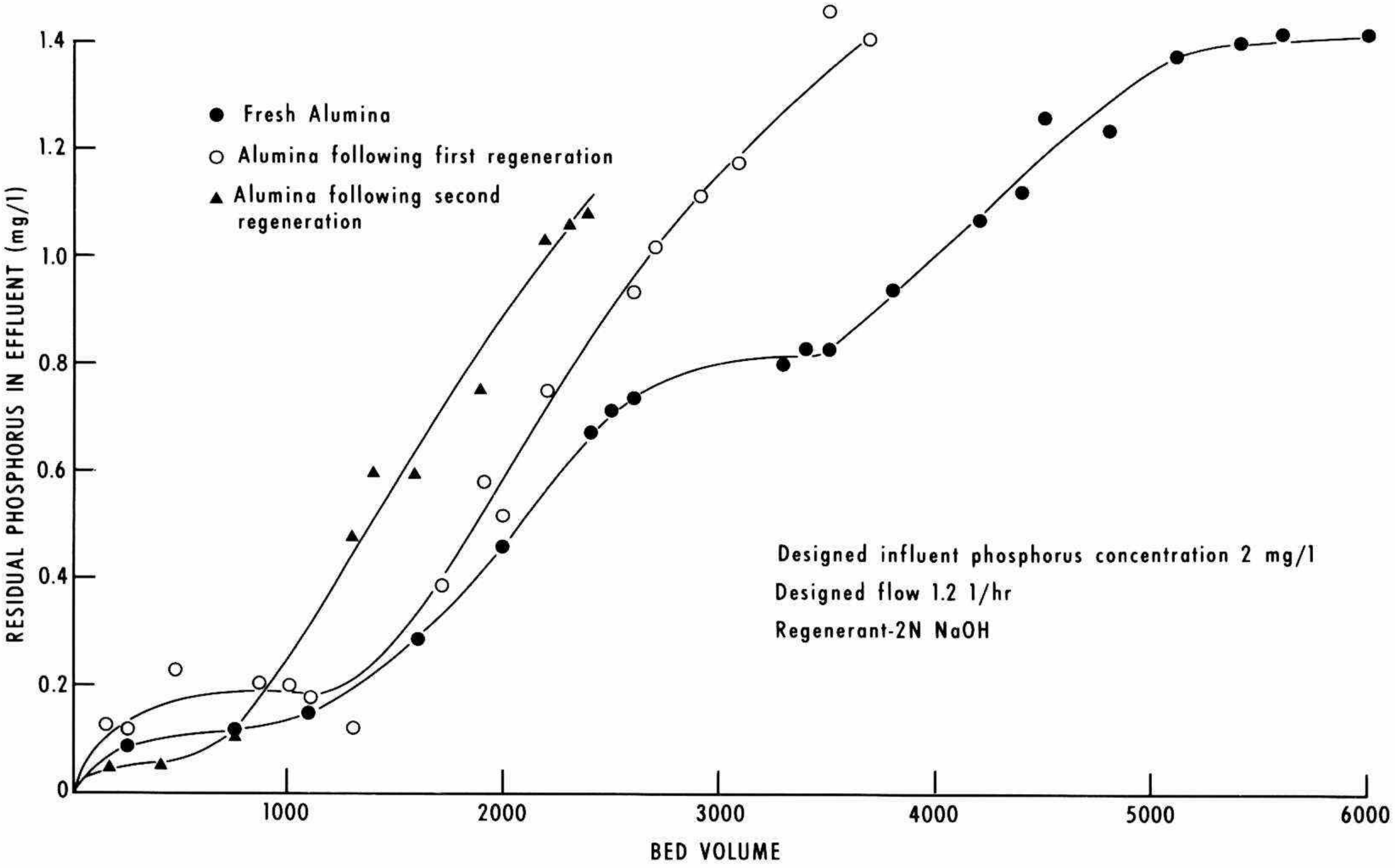

Figure 10 Effect of Regeneration on Activated Alumina Performance

TABLE 7. PHOSPHORUS BALANCE AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS - 1 mg/1

| PARAMETER DESCRIPTION | UNIT #1* | | | | UNIT #2** | | | |
|---|---|---|---|---|---|---|---|---|
| | Fresh Alumina | After First Regeneration | After Second Regeneration | Total | Fresh Alumina | After First Regeneration | After Second Regeneration | Total |
| I Operation of Columns | | | | | | | | |
| A Phosphorus in (mg) | 240 | 329 | 312 | 881 | 263 | 329 | 312 | 904 |
| B Phosphorus out (mg) | 58 | 130 | 101 | - | 77 | 145 | 111 | - |
| C Phosphorus adsorbed: A - B (mg) | 182 | 199 | 211 | 592 | 186 | 184 | 201 | 571 |
| D Alumina Capacity (mg P adsorbed/ gm $Al_2O_3$) | 6.0 | 6.6 | 7.0 | - | 6.6 | 6.5 | 7.1 | - |
| II Regeneration of Columns | | | | | | | | |
| A Phosphorus in Regenerant (mg) | 98 | 133 | 140 | - | 113 | 125 | 151 | - |
| B Phosphorus in Rinse Water (mg) | 1 | 54 | 40 | - | 1 | 36 | 33 | - |
| C Phosphorus Recovered: A + B (mg) | 99 | 187 | 180 | 466 | 114 | 161 | 184 | 459 |
| D Phosphorus Recovered: (Percent) | 54 | 94 | 86 | 79 | 61 | 88 | 92 | 80 |

* Unit #1 - Regenerated with 1N NaOH

** Unit #2 - Regenerated with 2N NaOH

When the alumina fed with 1 mg P/l was regenerated the percent phosphorus recovered during regeneration was 61% for 2N NaOH and 54% for 1N NaOH. For subsequent regeneration the percent phosphorus recovery was 90%, and the overall recovery for the three runs was 80%.

The results for influents with phosphorus concentrations of 2 mg/l are similar. The initial regeneration recovered 64% and 57% of the phosphorus when the regenerants were 2N and 1N NaOH, respectively. The second regeneration recovered 88%. In the third regeneration, more than 100% of the phosphorus was recovered. The phosphorus fed to the columns for the third run was less than half of that fed in the initial run (Table 8), but the regeneration was more rigorous; thus, some of the phosphorus from previous runs was recovered. Ames and Dean (1) reported the same phenomenon. The overall recovery of phosphorus for the three runs was about 88%.

### 5.1.4 Alumina losses

Alumina losses were estimated by measuring the concentrations of aluminum found in the regenerant and rinse waters. Such analyses probably included some alum flocs trapped in the columns. However, all the aluminum measured was calculated as alumina loss. The alumina from the columns was dried and weighed at the conclusion of the three runs. Extraneous material, however, had accumulated in the columns, and thus the alumina losses calculated by loss of weight were low (0 - 6%). The data from regeneration solutions were considered more realistic (Tables 9 and 10), and indicated losses less than those reported by Yee (10) (8% per cycle) and greater than those reported by Ames and Dean (1) (0.3% per cycle).

TABLE 8. PHOSPHORUS BALANCE AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS - 2 mg/l

| PARAMETER DESCRIPTION | UNIT #1* | | | | UNIT #2** | | | |
|---|---|---|---|---|---|---|---|---|
| | Fresh Alumina | After First Regeneration | After Second Regeneration | Total | Fresh Alumina | After First Regeneration | After Second Regeneration | Total |
| I Operation of Columns | | | | | | | | |
| A Phosphorus in (mg) | 366 | 240 | 150 | 756 | 406 | 240 | 150 | 796 |
| B Phosphorus out (mg) | 111 | 94 | 45 | - | 155 | 85 | 39 | - |
| C Phosphorus adsorbed: A - B (mg) | 255 | 146 | 105 | 506 | 251 | 155 | 111 | 517 |
| D Alumina Capacity (mg P adsorbed/ gm $Al_2O_3$) | 8.4 | 4.8 | 3.5 | - | 8.6 | 5.3 | 3.8 | - |
| II Regeneration of Columns | | | | | | | | |
| A Phosphorus in Regenerant (mg) | 143 | 90 | 135 | - | 157 | 107 | 141 | - |
| B Phosphorus in Rinse Water (mg) | 3 | 38 | 26 | - | 2 | 29 | 25 | - |
| C Phosphorus Recovered: A + B (mg) | 146 | 128 | 161 | 435 | 159 | 137 | 166 | 462 |
| D Phosphorus Recovered: (Percent) | 57 | 88 | 153 | 86 | 64 | 88 | 150 | 89 |

* Unit #1 - Regenerated with 1N NaOH

** Unit #2 - Regenerated with 2N NaOH

TABLE 9. ALUMINA LOSSES AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS - 1 mg/l

| | Losses as $Al_2O_3$ (gm) | |
|---|---|---|
| | 1N NaOH | 2N NaOH |
| Regeneration following run with fresh alumina | 1.29 | 1.14 |
| Regeneration following run with alumina regenerated once | 0.60 | 0.57 |
| Regeneration following run with alumina regenerated twice | 0.37 | 0.41 |
| Alumina losses for 3 regeneration (gm) | 2.26 | 2.12 |
| Total alumina loss for 3 regenerations (percent) | 7.4 | 7.5 |

## TABLE 10. ALUMINA LOSSES AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS - 2 mg/l

| | Losses as $Al_2O_3$ (gm) | |
|---|---|---|
| | 1N NaOH | 2N NaOH |
| Regeneration following run with fresh alumina | 0.75 | 0.92 |
| Regeneration following run with alumina regenerated once | 0.64 | 0.58 |
| Regeneration following run with alumina regenerated twice | 0.41 | 0.54 |
| Total alumina loss for 3 regenerations (gm) | 1.93 | 2.08 |
| Total alumina loss for 3 regenerations (percent) | 6.4 | 7.1 |

## 5.2 Phase II

### 5.2.1 Effect of flowrate on column performance

In the second phase of this program the effect of flowrate in the columns on the performance of activated alumina was investigated. The retention time was calculated from the flowrate and the volume of activated alumina in a non-fluidized column. The dry weight of alumina, in every case, was approximately 30 gm and the wet bed volume was measured to be 33 ml. When flow to the columns commenced, the alumina bed expanded and was partially fluidized. It is realized that this method of estimating the retention time in the column is only approximately indicative of the actual effluent/alumina contact time. When the concentration of phosphorus in the influent was 1 mg/l, flowrates of 0.6 l/hr (Table 11), 1.2 l/hr (Table 4) and 2.4 l/hr (Table 12) were compared (Figure 11). When the concentration of phosphorus in the influent was 2 mg/l, flowrates of 0.6 l/hr (Table 13) and 1.2 l/hr (Table 2) were evaluated.

Figure 11 clearly shows the effect of flowrate. As the flowrate through the columns was decreased from 2.4 to 0.6 l/hr, the plateau levels in the effluent decreased from 0.55 to 0.05 mg/l. However, the concentration of phosphorus in the effluent increased rapidly after 6000 bed volumes, in each case, indicating that the capacity of the activated alumina was being approached. Such a capacity corresponds to 6.5 mg P per gram of alumina. The data for the columns with a flowrate of 0.6 l/hr showed that the concentration of phosphorus in the effluent was less than 0.1 mg/l for approximately 3000 bed volumes. Lower flowrates would, presumably, lower the plateau below 0.1 mg P/l.

The effect of flowrate for the alumina column with an influent phosphorus concentration of 2 mg/l may be seen in Figure 12. It is evident that a slight improvement in the bed capacity occurs with the lower flowrate. At a flowrate of 0.6 l/hr, the phosphorus concentration in the column

TABLE 11. PERFORMANCE OF ACTIVATED ALUMINA COLUMN AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS IN MIXED SAMPLE OF 1 mg/l AND DESIGNED FLOW OF 0.6 l/hr

| SAMPLING TIME | | LENGTH OF RUN (Hours) | FLOW | | ORTHOPHOSPHATE CONCENTRATIONS | |
|---|---|---|---|---|---|---|
| Day | Hour | | Rate (l/hr) | Bed[Y] Volumes | Feed (mg P/l) | Effluent (mg P/l) |
| 1 | 11 am | 0 | 0.6 | | 1.00 | 0 |
| 1 | 12 am | 1 | 0.6 | 18 | | 0 |
| 1 | 4 pm | 5 | 0.6 | 88 | | 0 |
| 2 | 9 am | 22 | 0.6 | 390 | | 0.01 |
| 2 | 4 pm | 29 | 0.6 | 530 | | 0.04 |
| 3 | 9 am | 46 | 0.5 | 840 | | 0.03 |
| 3 | 3 pm | 52 | 0.5 | 950 | | 0.04 |
| 4 | 2 pm | 75 | 0.6 | 1400 | | 0.04 |
| 5 | 3 pm | 100 | 0.4* | 1800 | | 0.05 |
| 5 | 11 pm | 108 | 0.3* | 2000 | 1.00 | 0.05 |
| 6 | 9 am | 118 | 0.3* | 2100 | | 0.06 |
| 6 | 11 pm | 132 | 0.6 | 2400 | | 0.04 |
| 7 | 9 am | 142 | 0.6 | 2600 | | 0.06 |
| 7 | 1 pm | 146 | 0.7 | 2700 | | 0.09 |

Y Weight of Alumina - 30.00 gm

* Flow Rate Adjusted to 0.6 l/hr

TABLE 11. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 0.6 l/hr

| SAMPLING TIME | | LENGTH OF RUN (Hours) | FLOW | | ORTHOPHOSPHATE CONCENTRATIONS | |
|---|---|---|---|---|---|---|
| Day | Hour | | Rate (l/hr) | Bed Y Volumes | Feed (mg P/l) | Effluent (mg P/l) |
| 7 | 11 pm | 156 | 0.6 | 2800 | 1.00 | 0.11 |
| 8 | 9 am | 166 | 0.6 | 3000 | | 0.11 |
| 8 | 5 pm | 174 | 0.6 | 3200 | | 0.12 |
| 8 | 12 pm | 181 | 0.6 | 3300 | | - |
| 9 | 9 am | 190 | 0.6 | 3500 | | 0.18 |
| 9 | 1 pm | 194 | 0.6 | 3500 | | 0.18 |
| 9 | 3 pm | 196 | 0.6 | 3600 | | 0.16 |
| 9 | 11 pm | 204 | 0.6 | 3700 | | 0.22 |
| 10 | 9 am | 214 | 0.6 | 3900 | | 0.25 |
| 10 | 1 pm | 218 | 0.6 | 4000 | 1.00 | 0.23 |
| 10 | 5 pm | 222 | 0.6 | 4000 | | 0.20 |
| 10 | 12 pm | 229 | 0.6 | 4200 | | 0.26 |
| 11 | 3 pm | 244 | 0.7 | 4400 | | 0.29 |
| 11 | 11 pm | 252 | 0.6 | 4600 | | 0.30 |

Y Weight of Alumina - 30.00 gm
* Flow Rate Adjusted to 0.6 l/hr

TABLE 11. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 0.6 l/hr

| SAMPLING TIME | | LENGTH OF RUN | FLOW | | ORTHOPHOSPHATE CONCENTRATIONS | |
|---|---|---|---|---|---|---|
| Day | Hour | (Hours) | Rate (l/hr) | Bed Y Volumes | Feed (mg P/l) | Effluent (mg P/l) |
| 12 | 1 pm | 266 | 0.6 | 4800 | 1.00 | 0.32 |
| 13 | 9 am | 286 | 0.6 | 5200 | | 0.34 |
| 13 | 5 pm | 294 | 0.6 | 5300 | | 0.37 |
| 14 | 9 am | 310 | 0.6 | 5600 | | 0.40 |
| 14 | 4 pm | 317 | 0.6 | 5800 | | 0.43 |
| 15 | 9 am | 334 | 0.6 | 6100 | | 0.45 |
| 15 | 5 pm | 342 | 0.6 | 6200 | 1.03 | 0.48 |
| 16 | 9 am | 358 | 0.5* | 6500 | | 0.47 |
| 16 | 5 pm | 366 | 0.6 | 6700 | | 0.51 |
| 17 | 9 am | 382 | 0.6 | 6900 | | 0.61 |
| 17 | 12 am | 385 | 0.6 | 7000 | | 0.61 |
| 17 | 4 pm | 389 | 0.6 | 7100 | | 0.62 |
| 18 | 10 am | 407 | 0.6 | 7400 | | 0.68 |
| 18 | 8 pm | 417 | 0.6 | 7600 | | 0.69 |

Y Weight of Alumina - 30.00 gm
* Flow Rate Adjusted to 0.6 l/hr

TABLE 11. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 0.6 l/hr

| SAMPLING TIME | | LENGTH OF RUN (Hours) | FLOW | | ORTHOPHOSPHATE CONCENTRATIONS | |
|---|---|---|---|---|---|---|
| Day | Hour | | Rate (l/hr) | Bed Volumes[Y] | Feed (mg P/l) | Effluent (mg P/l) |
| 19 | 12 am | 433 | 0.6 | 7900 | 1.08 | 0.76 |
| 19 | 11 pm | 444 | 0.6 | 8100 | | 0.76 |
| 20 | 9 am | 454 | 0.6 | 8300 | | 0.75 |

[Y] Weight of Alumina - 30.00 gm
* Flow Rate Adjusted to 0.6 l/hr

TABLE 12. PERFORMANCE OF ACTIVATED ALUMINA COLUMN AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS IN MIXED SAMPLE OF 1 mg/l AND DESIGNED FLOW OF 2.4 l/hr

| SAMPLING TIME | | | LENGTH OF RUN (Hours) | FLOW | | ORTHOPHOSPHATE CONCENTRATIONS | |
|---|---|---|---|---|---|---|---|
| Day | Hour | | | Rate (l/hr) | Bed Volumes * | Feed (mg P/l) | Effluent (mg P/l) |
| 1 | 10 | am | 0 | 2.4 | | 1.01 | 0 |
| 1 | 1 | pm | 3 | 2.3 | 220 | | 0.04 |
| 1 | 4 | pm | 6 | 2.2 | 430 | | 0.04 |
| 1 | 11 | pm | 13 | 2.3 | 930 | | 0.06 |
| 2 | 9 | am | 23 | 2.3 | 1700 | | 0.21 |
| 2 | 5 | pm | 31 | 2.4 | 2200 | | 0.25 |
| 2 | 12 | pm | 38 | 2.4 | 2700 | 1.06 | 0.31 |
| 3 | 9 | am | 47 | 2.4 | 3400 | | 0.52 |
| 3 | 1 | pm | 51 | 2.3 | 3700 | | 0.34 |
| 3 | 3 | pm | 53 | 2.4 | 3800 | | 0.31 |
| 3 | 11 | pm | 61 | 2.4 | 4400 | | 0.45 |
| 4 | 9 | am | 71 | 2.4 | 5100 | | 0.54 |
| 4 | 1 | pm | 75 | 2.4 | 5400 | 1.00 | 0.54 |

* Weight of Alumina - 30.00 gm

TABLE 12. (CONT'D)

Designed Influent Concentration of Phosphorus in Mixed Sample - 1 mg/l
Designed Flow - 2.4 l/hr

| SAMPLING TIME | | LENGTH OF RUN (Hours) | FLOW | | ORTHOPHOSPHATE CONCENTRATIONS | |
|---|---|---|---|---|---|---|
| Day | Hour | | Rate (l/hr) | Bed Volumes * | Feed (mg P/l) | Effluent (mg P/l) |
| 4 | 5 pm | 79 | 2.4 | 5700 | 1.00 | 0.53 |
| 4 | 12 pm | 86 | 2.4 | 6200 | | 0.65 |
| 5 | 3 pm | 101 | 2.4 | 7300 | | 0.77 |
| 5 | 11 pm | 109 | 2.4 | 7800 | | 0.79 |

* Weight of Alumina - 30.00 gm

TABLE 13. PERFORMANCE OF ACTIVATED ALUMINA COLUMN AT DESIGNED INFLUENT CONCENTRATION OF PHOSPHORUS IN MIXED SAMPLE OF 2 mg/l AND DESIGNED FLOW OF 0.6 l/hr

| SAMPLING TIME | | LENGTH OF RUN (Hours) | FLOW | | ORTHOPHOSPHATE CONCENTRATIONS | |
|---|---|---|---|---|---|---|
| Day | Hour | | Rate (l/hr) | Bed* Y Volumes | Feed (mg P/l) | Effluent (mg P/l) |
| 1 | 11 am | 0 | 0.6 | 0 | 2.05 | 0 |
| 1 | 12 am | 1 | 0.6 | 19 | | 0.02 |
| 1 | 4 pm | 5 | 0.6 | 97 | | 0.04 |
| 2 | 9 am | 22 | 0.7 | 430 | | 0.09 |
| 2 | 11 am | 24 | 0.7 | 470 | | 0.09 |
| 2 | 4 pm | 29 | 0.6 | 560 | | 0.07 |
| 3 | 9 am | 46 | 0.6 | 890 | | 0.08 |
| 3 | 4 pm | 52 | 0.7 | 1000 | | 0.10 |
| 4 | 2 pm | 75 | 0.7 | 1500 | | 0.17 |
| 5 | 3 pm | 100 | 0.7 | 1900 | | 0.48 |
| 5 | 11 pm | 108 | 0.7 | 2100 | | 0.60 |
| 6 | 9 am | 118 | 0.6 | 2300 | | 0.63 |
| 6 | 5 pm | 126 | 0.6 | 2400 | | 0.63 |

Y Weight of Alumina - 30.00 gm

* Bed Volumes calculated assuming an average flow of 0.64 l/hr

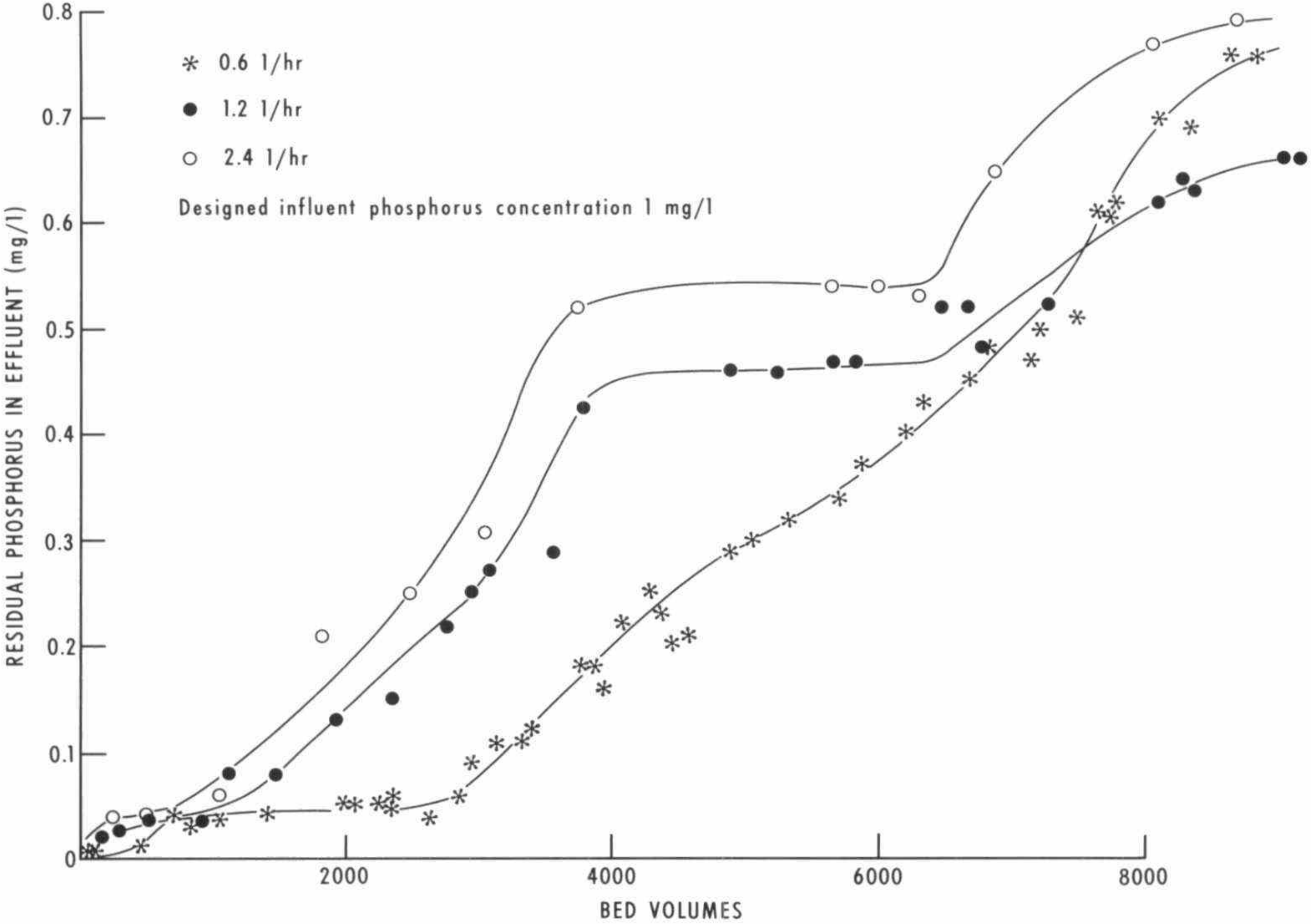

Figure 11 Effect of Flow on Activated Alumina Performance

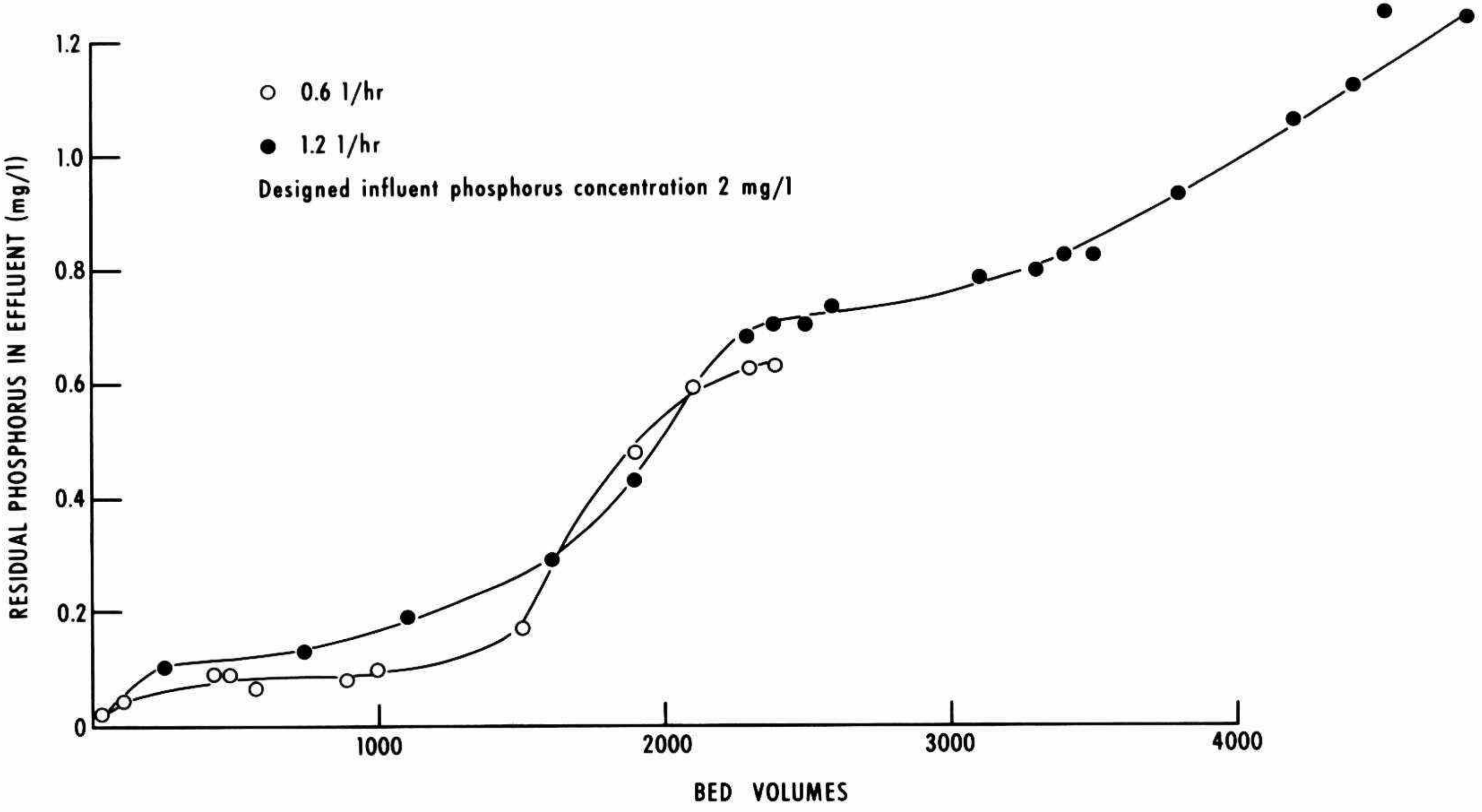

Figure 12 Effect of Flow on Activated Alumina Performance

effluent was less than 0.1 mg/l for at least 1000 bed volumes. It may therefore be concluded that, if a full scale process is designed to treat 1 mg/l average secondary effluent phosphorus concentrations, infrequent higher phosphorus concentrations would not adversely affect the quality of the tertiary effluent from the activated alumina column.

The study was primarily concerned with establishing the feasibility of activated alumina columns as a tertiary treatment process for waste treatment plants. The data obtained, however, also supported kinetic studies of activated alumina-phosphorus reactions such as those by Neufeld and Thodos (5) who reported three reaction plateaus when the flowrate in the columns was sufficiently slow.

In the present study, the 1 mg P/l influent data at three flowrates were plotted on an expanded scale as shown in Figure 13. A series of plateaus were revealed similar to those described by Neufeld and Thodos. These plateaus became less defined as the flowrate was increased.

### 5.2.2 Economic feasibility

The process under consideration involved reducing the phosphorus in raw sewage to 1 mg/l by alum followed by treatment in activated alumina columns. The phosphorus concentrations in the polished effluent of 0.5, 0.2 and 0.1 mg/l were arbitrarily selected for the purpose of establishing process cost estimates. As a comparison, cost estimates for treatment by alum alone were developed even though there was some doubt that alum treatment could produce a phosphorus effluent concentration with less than 0.1 mg/l 80% of the time (Table 14). In estimating the costs for the combination alum-activated alumina process, the experimental results of the present study were utilized to estimate the quantities of chemicals required. However, data from literature were used whenever the corresponding data from this study were not available. In calculating the parameters for Table 14,

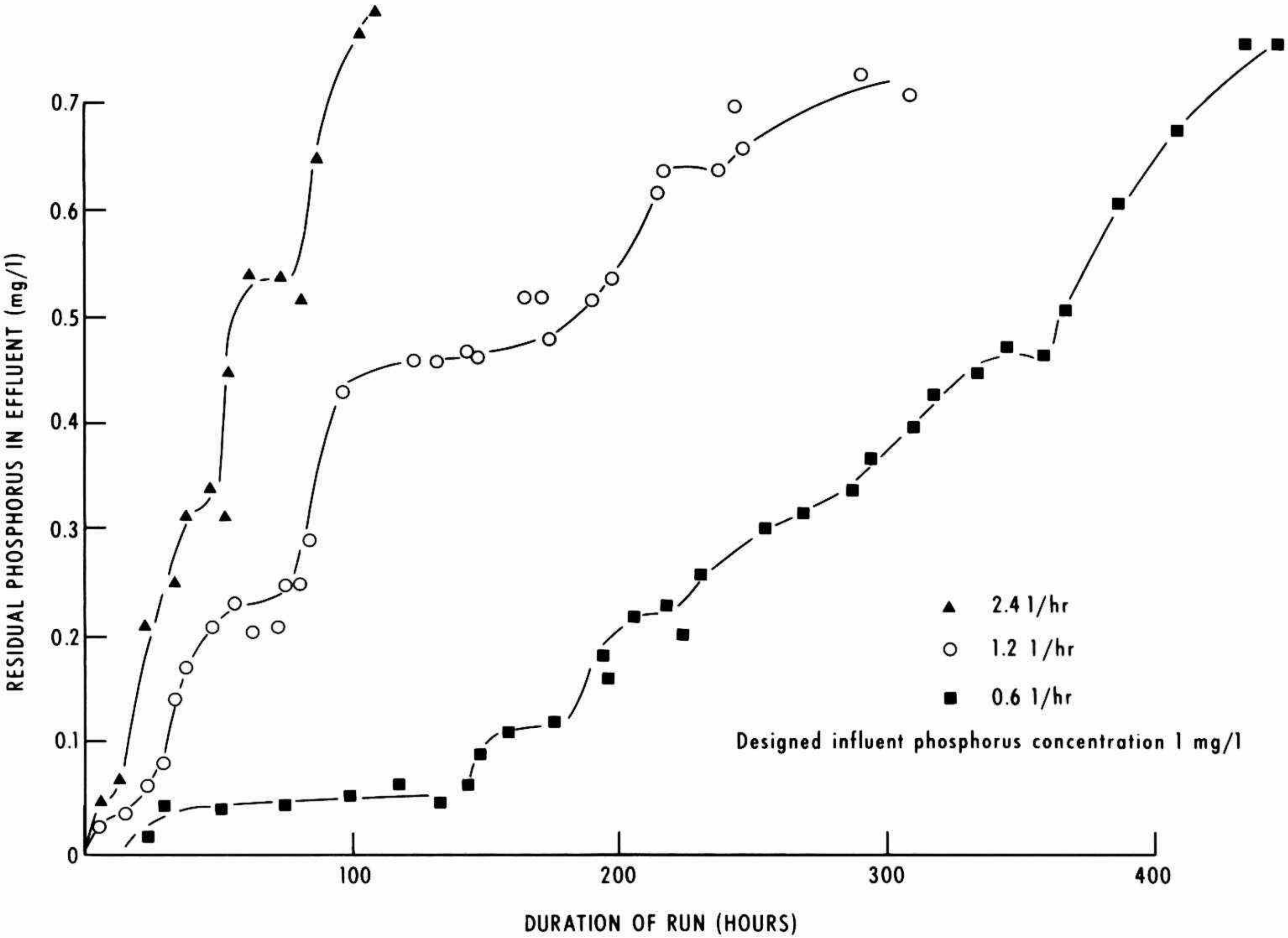

Figure 13 Illustration of Plateau Concentration in Column Effluents

loss of alumina per regeneration cycle was assumed to be 5 percent. Data indicated approximately 7.5 percent alumina losses over three regeneration cycles and, therefore, the 5 percent figure assumed for each cycle is considered to be conservative. Less alumina and, hence, lower pound losses per cycle would be quite likely. Thirty-five bed volumes of 1N sodium hydroxide were assumed necessary to regenerate the activated alumina with a 5% loss of sodium hydroxide per cycle; Ames and Dean (1) found eight bed volumes sufficient, and the present study indicated that contact time between the activated alumina and regenerant could be significant. No nitric acid was assumed necessary. Further, it was recognized that the sodium hydroxide solution must be regenerated in order to avoid a disposal problem and to reduce costs to a practical level. Ames and Dean (1) discussed in detail the costs of precipitating the phosphorus from sodium hydroxide solutions with lime, and indicated that the resulting volume of calcium phosphate sludge was small. These cost data, however, were dated 1970 and thus new parameters were developed using present day prices (Table 14).

The cost estimates in Table 14 indicate that a combination of alum and activated alumina is more economical if the desired phosphorus concentration in the tertiary effluent is less than 0.5 mg/l.

TABLE 14. ECONOMIC JUSTIFICATION.

| Phosphorus Removal | Cost of Alum Precipitation per 1 MIG Treated | | Cost of Activated Alumina Process per 1 MIG Treated | |
|---|---|---|---|---|
| | Operating Cost | Capital Cost | Operating Cost | Capital Cost |
| From 1 - 0.5 mg/l | $12.92 | $ 0 | $11.43 | $25,000 |
| From 1 - 0.2 mg/l | $33.85 | $65,000 | $18.88 | $48,000 |
| From 1 - 0.1 mg/l | $60.70 | $100,000 | $20.87 | $73,000 |

NOTES: The estimates for operating costs of the alum precipitation process is based on:

- Jar test results conducted on final effluent from the Oakville Water Pollution Control Plant.
- Cost of $0.32 per lb of aluminum.
- Cost of $1.25 per disposal of 1 cubic yard of sludge.

The estimate for capital cost of alum precipitation is based on the assumption that for lower than 0.5 mg/l of phosphorus in the treated effluent an effluent polishing filter would be required.

The estimate for the operating cost of the activated alumina process is based on:

- Nominal retention time of 1.5, 5 and 10 minutes in the columns, respectively, according to the required phosphorus level in the final effluent.
- 5% alumina loss per each regeneration cycle with sodium hydroxide and cost of $0.29 per lb for activated alumina.
- 5% sodium hydroxide loss per each regeneration cycle at a cost of $0.022 per lb of sodium hydroxide.
- Cost of $0.012 per lb of lime.
- Disposal cost of $1.25 per cubic yard of sludge.

# BIBLIOGRAPHY

1. AMES, L.L. and DEAN, R.B., J.W.P.C.F. 42, #5, Part 2 R161 (1970)
2. CHURMS, S.C., J.S. African Chem. Inst. 19, 98 (1966)
3. Guidelines For Treatability Studies For Phosphorus Removal
4. KUBLI, H., Helv. Chem. Acta 3, 453 (1947)
5. NEUFELD, R.D. and THODOS, G., Environ. Sci. & Technol. 3 661 (1969)
6. SCHWAB, G., Dis. Faraday Soc. 7, 170 (1949)
7. SHIBATA, M., Science (Japan) 19, 570 (1949)
8. SHUVAERVA, G.M. and GAPON, E.N., Zhur. Anal. Khim. (U.S.S.R.) 8, 50 (1953)
9. SINHA, P.R., and CHOUDBURY, A.K. J. Indian Chem. Soc. 31, 211 (1954)
10. YEE, W.G., J. Am. Water Works Ass'n. 58 239 (1966)

# ABBREVIATIONS

| | |
|---|---|
| Al | Aluminum |
| $Al_2O_3$ | Alumina |
| gm | Gram |
| gal | Imperial Gallon |
| hr | Hour |
| mg/l | Milligrams per Litre |
| mμ | Millimicrons |
| ml | Millilitre |
| MIG | Million Imperial Gallons |
| min | Minutes |
| P | Phosphorus |
| lb | Pounds |
| NaOH | Sodium Hydroxide |
| W.P.C.P. | Water Pollution Control Plant |

# APPENDIX

# ANALYTICAL METHOD FOR PHOSPHORUS DETERMINATION

## A. Determination of Total Phosphorus (acid-hydrolyzable)

(1) A suitable aliquot of thoroughly mixed sample (depending on the expected phosphorus concentration) is measured out into a beaker and diluted to approximately 60 ml.

(2) Then 2 drops of phenolphthalein indicator are added. If red colour develops, strong acid solution (600 ml concentrated $H_2SO_4$ plus 4 ml concentrated $HNO_3$ diluted to 1 litre) is added to just discharge the colour. Then boiling chips and an additional 0.5 ml of strong acid solution is added, and the beaker is covered with a watch glass and boiled for 90 minutes at $400^oF$. The volume of the solution is maintained between 30 and 60 ml.

(3) The boiled solution is cooled, 6N NaOH added until the solution turns pink, and titrated with dilute $H_2SO_4$ until the colour is just eliminated.

(4) The neutralized solution is transferred quantitatively to a 100 ml volumetric flask and made up to volume.

(5) 4 mls of ammonium molybdate solution,
(25 gm $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ plus 280 ml concentrated $H_2SO_4$ in 1 litre) and 6 drops stannous chloride solution,
(2.5 gm $SnCl_2 \cdot 2H_2O$ in 100 ml glycerol) are added and the colour developed for 10 minutes.

(6) The absorbence is read on a Spectrophotometer at a wave length of 690 mμ.

(7) The concentration of total phosphorus is read from the calibration curve.

B. Determination of Total Soluble Phosphorus (filtrable)

The sample is filtered through Sartorius membrane filters and a suitable aliquot of filtrate is taken for determination. Then the procedure outlined under A. is followed.

C. Determination of Orthophosphate

(1) A suitable aliquot of thoroughly mixed sample is measured out in 100 ml volumetric flask, pH adjusted to neutral, if necessary, and made up to volume.

(2) 4 mls of ammonium molybdate solution, (25 gm $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ plus 280 ml concentrated $H_2SO_4$ in 1 litre) and 6 drops stannous chloride solution, (2.5 gm $SnCl_2 \cdot 2H_2O$ in 100 ml glycerol) are added and the colour developed for 10 min.

(3) The absorbence is read on a Spectrophotometer at a wave length of 690 mμ.

(4) The concentration of orthophosphate as phosphorus is read from the calibration curve.

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Effluent polishing by filtration
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